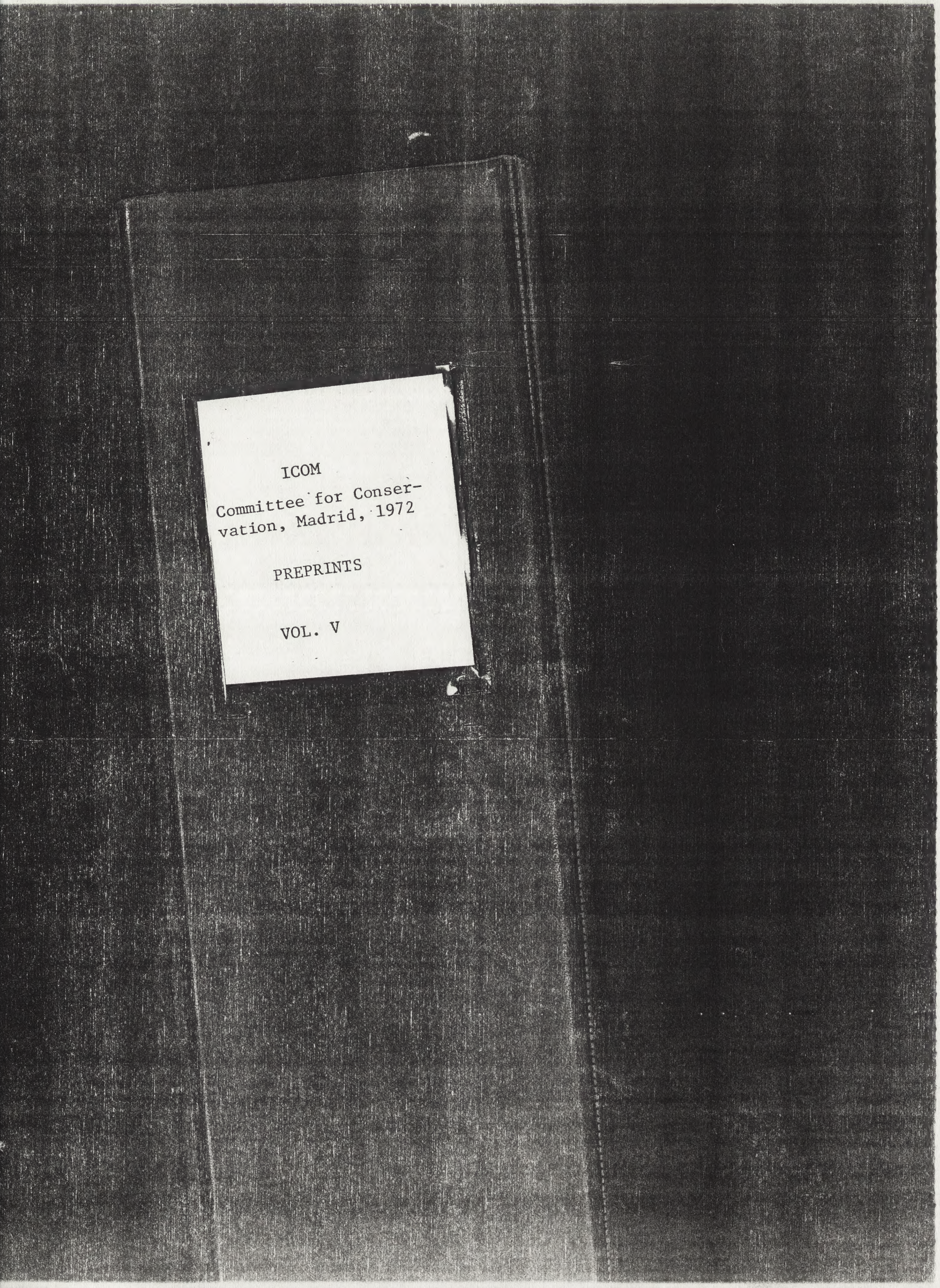

ICOM

Committee for Conservation, Madrid, 1972

PREPRINTS

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The International Council of
Museums -
Committee for Conservation

Conseil International des
Musées
Comité pour la Conservation

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M. Jean Bouis (Coordinateur)

LES PROBLEMES TECHNIQUES PARTICULIERS DE LA CONSERVATION DANS LES FOUILLES SOUS-MARINES

Salomon Reinach a déclaré, il y a longtemps déjà, que le fond de la mer recelait "le plus riche musée du Monde Antique". Mais à cette époque, les moyens de prospection sub-aquatiques étaient primitifs et mal adaptés à une fouille scientifique.

Depuis une vingtaine d'années, grâce à l'invention du scaphandre autonome de J.Y. Cousteau et aux nombreux perfectionnements qui lui ont été apportés, l'homme peut se déplacer et travailler en milieu marin à peu près aussi librement que sur terre. Et les paroles du vieil historien sont plus que confirmées : les portes du "plus riche musée" sont maintenant ouvertes aux archéologues, qui peuvent inventorier ses réserves particulièrement riches.

Mais l'homme-plongeur peut aussi, parfois, détruire ces vestiges irremplaçables, par maladresse, par vandalisme, ou, plus simplement, par l'appat du gain que représente, de nos jours, la commercialisation d'objets authentiques et souvents intacts. La conservation de ce "Musée" et des objets qu'il renferme pose donc une série de problèmes parfois inédits, généralement très différents de ceux rencontrés à l'occasion des fouilles terrestres et dont l'étude entre parfaitement, croyons-nous, dans le cadre des activités de l'ICOM.

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La fouille archéologique sous-marine n'est évidemment qu'un aspect de l'Archéologie Générale : le but essentiel est de retrouver les divers moments de l'histoire de l'Homme. L'archéologie ne saurait être réduite à la fouille, qui n'est qu'une étape, la plus excitante peut-être, du travail de l'archéologue. Mais nous limiterons notre propos à cette étape, laissant aux historiens le long travail d'interprétation et d'étude qui est l'objet final de la Recherche Archéologique.

Le milieu sub-aquatique, qu'il soit marin ou lacustre, est fondamentalement différent du milieu aérien. La maintenance des matériaux au cours des âges n'a pas suivi le même processus: certains éléments ont complètement disparu, comme par exemple, les matières organiques animales ou végétales; d'autres, et notamment les objets en fer, sont transformés dans leur structure interne, mais leur forme sont souvent maintenues; d'autres, enfin, sont remarquablement bien conservés et nous apportent des témoins intacts que l'on trouve très rarement dans des fouilles terrestres : c'est le cas des céramiques, de beaucoup de métaux non ferreux, des matériaux pierreux.

Cependant, d'une manière générale, leur pérénité à l'air libre, leur conservation muséographique demanderont des traitements plus ou moins complexes avant qu'ils soient définitivement stabilisés.

L'intérêt particulier de la fouille sous-marine est d'apporter des renseignements, de fournir des objets que l'on ne trouvera nulle part ailleurs. Elle est seule à permettre l'étude de la construction navale, des techniques de navigation, de la réalisation des ports, et, par conséquent, des méthodes de commerce dans l'antiquité. Sur ces sujets, l'épigraphie, les documents textuels ou les figures sont extrêmement rares et toujours insuffisants.

Même pour la connaissance des moyens usuels d'une civilisation, la fouille sous-marine est inestimable: le gisement est presque toujours une épave de navire, c'est-à-dire un ensemble de matériel (coque, agrès, objets d'usage courant, cargaison, etc.....) en synchronisme parfait. C'est une "tranche de vie" qui s'est figée pour l'éternité. Sur terre, l'équivalent ne peut se rencontrer que dans une grande sépulture (et à condition qu'elle n'ait pas été violée) et encore le mobilier des tombes correspond plus souvent à des traditions funéraires qu'à la vie courante !

C'est en mer que l'on a découvert quelques objets d'art qui comptent parmi les plus précieux de ceux que nous a légué l'Antiquité. La typologie des objets les plus courants (amphores, vaisselle, etc.....) ne peut être établie que par l'étude des cargaisons de navires. Le transport des matières pondéreuses le long des voies commerciales de l'antiquité Greco-Italique était toujours maritime. De nombreuses épaves contiennent des lingots, précieux témoins de la métallurgie de l'époque. D'autres recèlent des matériaux de construction: blocs de marbre, tuiles, mosaîques, statues et colonnes déjà taillées, ou même des sarcophages attendant la gravure de leur dédicace.

Dans tous les cas, les objets que l'on remonte à la surface sont dans un état satisfaisant, parfois voisin du "neuf", sous réserve de quelques dépots de concrétions diverses qu'il sera, en général, facile d'éliminer.

Enfin, la fouille sous-marine présente un avantage que l'on ne perçoit pas toujours: elle permet d'éviter le "drame de conscience" de beaucoup de fouilleurs qui considèrent, à juste titre, qu'attaquer une zone archéologique, fouiller un habitat ou une nécropole, faire seulement un sondage, c'est abimer, parfois supprimer les indices du passage ou de l'installation des hommes, c'est détruire ce que l'on ne retrouvera plus: un environnement qui ne sera jamais vraiment reconstitué! En mer, ce risque ne peut éxister puisqu'une épave est, par nature, étrangère au site dans lequel on la retrouve, et on peut sans danger la récupérer intégralement. Il serait même idéal que l'on puisse reconstituer le navire et son chargement en un milieu plus facilement accessible!

Il est donc indiscutable que, pour l'historien, ce genre de fouille est du plus grand intérêt et que, lorsque les moyens techniques seront suffisamment perfectionnés, l'exploitation systématique des gisements sub-aquatiques apportera à l'humanité une contribution exceptionnelle à la connaissance des civilisations antiques ou médiévales.

Cependant,avant que l'historien ou le Musée prennent possession de cette riche moisson, il sera toujours nécessaire que le laboratoire et les techniciens réalisent un certain nombre d'interventions qui sont, chronologiquement :

- La prospection des fonds et la détermination précise des sites;
- Le dégagement de l'épave et de sa cargaison des matériaux hétérogènes qui la recouvrent presque toujours;
- Le relevé planimétrique soigné de l'ensemble du site, devant permettre par la suite la reconstitution de l'architecture navale et du chargement;
- L'exploitation du site par la récupération controlée de tous les objets;
- Enfin, et surtout, le traitement de conservation et parfois de restitution de ces objets après leur émersion afin d'obtenir leur stabilisation définitive.

Chacune de ces opérations mettra en oeuvre des techniques souvent originales, dont beaucoup sont encore au niveau de l'expérimentation. L'examen et la confrontation de ces techniques constituent le but et le programme que se propose le Groupe de Travail consacré aux ETUDES et RECHERCHES CONCERNANT les FOUILLES SOUS-MARINES.

Afin de mieux faire apprécier la compléxité des problèmes posés, nous allons développer succintement les différents postes de ce programme.

La prospection des fonds est indispensable pour déterminer l'emplacement exact d'une épave homogéne et compléte non encore pillée par les amateurs. Cette épave sera, d'une manière générale, située à une profondeur comprise entre 20 et 45 m. de profondeur, sur un fond de sable. A une profondeur inférieure, il est à peu prés impossible de retrouver des vestiges assemblés, car les mouvements de la mer pendant les tempétes, les marées ou les courants ont brisé le navire et dispersé sa cargaison. On retrouve quelque fois des éléments lourds, notamment des lingots ou des piéces métalliques, qui se sont coincés contre des rochers, mais ces découvertes fortuites sont alors éloignées de tout contexte.

De plus, les pécheurs et, de plus en plus fréquemment, les touristes ont déjà ramassé presque tous les objets qui ont pu résister aux mouvements marins.

D'autre part, la profondeur de 45m. est une limite imposée par les conditions physiologiques de la plongée. Au delà de 40 m., le plongeur risque des accidents dus, en particulier, à la narcose. Et la durée possible de travail au fond est d'autant plus courte que la profondeur est grande: un plongeur pourra rester immergé une demi-heure à 30 m., mais il ne séjournera que 5 minutes à 60 m. s'il veut éviter de longs "paliers de décompression" lors de la remontée. Le temps que chaque chercheur pourra passer sur un chantier sous-marin est donc bref et il ne pourra faire que 2 plongées par jour au maximum.

L'épave sera presque toujours recouverte de sable, ou de vase, et quelques fois de végétaux marins. Elle sera donc peu visible et, en fait, la quasi totalité des épaves connues ont été découvertes par hasard, par des plongeurs se promenant pour leur plaisir ou à la recherche d'un banc de poisson!

En Grèce, en Turquie, en Tunisie, ce sont souvent les pécheurs d'éponges professionnels, équipés de scaphandres lourds qui ont été à l'origine des découvertes les plus importantes. La prospection réalisée dans ces conditions est évidemment très aléatoire, et il serait souhaitable qu'elle soit effectuée d'une manière plus systématique, avec des moyens plus scientifiques.

Pour cela, on a essayé de promener sur les fonds une caméra de télévision ou des engins d'observation sous-marine (Tourelle Galeazzi, sous-marin de poche, etc...) mais les résultats sont médiocres en raison de la visibilité restreinte (de l'ordre de 15 à 20 mètres dans les meilleures conditions), et ils ne sont à l'échelle du prix de revient des équipements mis en oeuvre.

On étudie actuellement l'application des techniques modernes : les sondeurs ultrasoniques, les "sonars" à effet horizontal, les gravimètres qui déterminent les variations de la pesanteur en fonction de la rupture d'homogénéité des sols, enfin le magnétomètre à protons qui mesure les distorsions du champ magnétique terrestre .

Monsieur Donald A. Frey, professeur au laboratoire de recherches archéologiques d'Oxford, doit nous communiquer lors de la réunion de Madrid d'octobre 1972 les résultats des essais de magnétomètres qu'il réalise cette année sur plusieurs gisements en exploitation.

Le dégagement d'une épave qui a été répérée au cours de la prospection est un travail de nettoyage de la surface du tumulus par l'enlèvement des dépôts qui se sont accumulés au cours des siècles. Il y a intérêt à dégager la plus grande surface possible, au mieux toute la partie encore visible du navire.

Mais ce travail de "terrassier de la mer" est rendu d'autant plus difficile que le déplacement sans précaution, dans l'eau, de matériaux à très fine granulométrie provoque de véritables "nuages" qui réduisent à néant la visibilité.

Pour éviter ce phénomène particulièrement génant, on utilise un engin "suceuse" constitué essentiellement par un tuyau fléxible, de forte section (100 à 200 mm. de diamètre), remontant jusqu'à la surface de la mer et débouchant dans un caisson. A la base de ce tube, une injection d'air comprimé provoque l'émulsion de l'eau qui, par différence de densité, s'élève rapidement dans le tuyau, créant une aspiration d'autant plus forte que la profondeur est grande. Cette aspiration est parfois si violente que non seulement la vase et le sable sont emportés mais également des petits objets (monnaies, poteries, tessons divers) qu'il y aurait intérêt à maintenir en place.

Toutefois, la suceuse est à peu près inopérante sur une vase comptacte ou sur un herbier. On lui associe alors des lances à eau, à forte pression, qui arrivent à déliter des masses de concrétions, mais qui bien souvent brisent ou déplacent le matériel archéologique.

Les procédés actuels de dégagement ne sont donc pas très au point, et nous nous proposons d'étudier leur amélioration.

Le relevé planimétrique du site doit suivre rapidement le dégagement et précéder tout enlèvement de mobilier. Les méthodes de relevés varient suivant l'objet étudié. Si l'on cherche à établir le plan de constructions immergées (un port par

ex.) se trouvant à faible profondeur, on peut utiliser la photographie aérienne et les procédés employées en cartographie.

Le relevé d'une épave cause des problèmes plus complexes: la restitution d'un ensemble d'objets séparés doit être valable dans les trois dimensions et pouvoir se substituer à une statigraphie par plans de niveaux successifs qui est impossible en milieu marin.

En général, on matérialise sur l' épave un cadrillage à mailles assez serrées (1 x 1 m. ou 2 x 2 m.) qui peut être constitué par des cordages souples ou par un cadre métallique rigide (qui est nettement préférable). En photographiant successivement tous les carrés, on établira assez facilement un plan valable de l'épave, sur lequel seront portées les mesures verticales prises à la main par rapport à un niveau de référence.

Une méthode plus scientifique de relevés stéréophotographiques est actuellement expérimentée, dont l'ambition est de réaliser une étude photogrammétrique directe des épaves. Mais elle rencontre certaines difficultés, en raison de la réfraction de l'eau et aussi d'une mauvaise adaptation aux conditions de la fouille sous-marine du matériel de restitution nécessaire pour intégrer et traduire les données stéréogrammatiques . Nous nous proposons de collationner les différents essais de cette méthode et de mettre en rapport les chercheurs qui la pratiquent afin de contribuer à son perfectionnement.

La récupération des objets, c'est-à-dire la fouille proprement dite, ne met pas en oeuvre des techniques très différentes de celles des fouilles terrestres. Les difficultés rencontrées sont généralement inérentes aux conditions de la plongée et ne sont donc pas du ressort de nos travaux.

Cependant, certains cas particuliers rendent necessaire l'emploi d'engins conçus spécialement par l'esprit inventif des fouilleurs, et nous nous proposons d'assurer la diffusion de ces "trouvailles" afin de constituer une somme technologique et de la mettre à la disposition de tous les chercheurs.

Lorsque la cargaison, le mobilier, le matériel de navigation, et même parfois des éléments de coque ont été ramenés à l'air libre, il est indispensable, pour assurer leur

conservation, de les traiter en laboratoire.

Même les céramiques les plus stables, les amphores, doivent subir, au moins, un long rinçage à l'eau douce pour éliminer tous les sels et les organismes de la microfaune qui les ont imprégnés pendant leur séjour en milieu marin.

Certains matériaux (les bois notamment) ont subi des modifications physico-chimiques de la structure même de la matière qui les compose, et des Groupes de travail sont déjà spécialisés dans leur étude (Bois gorgés d'eau, Matériaux Pierreux etc......).

Mais tous les objets ayant séjourné dans la mer sont nécessairement chlorurés, ceux provenant des lacs et des rivières ont subi l'action des bactéries sulfatantes. Les sels résultants de l'inclusion de ces éléments chimiques dans le matériau doivent être éliminés, ou neutralisés, ou compensés, par des produits de fixation susceptibles de rendre leur présence compatible avec les conditions normales de la conservation muséographique.

De nombreuses recherches sont entreprises, qui n'ont pas toutes encore abouti à des résultats pratiques. Nous avons, là aussi, l'intention de coordonner les travaux des chercheurs déjà nombreux qui ont bien voulu apporter leur collaboration à notre Groupe de Travail.

Au cours de la Réunion de Madrid nous pourrons constituer des équipes de techniciens qui se spécialiseront sur un des problèmes que nous venons d'évoquer. Un programme sera établi pour les prochaines années.

Et nous espérons que, dans des délais relativement brefs, nous pourrons :

- Créer des règles de technologie valables et expérimentées, qui font actuellement totalement défaut;
- Mettre à la disposition de tous (techniciens, historiens, conservateurs de musée, etc.....) une documentation comparative des différentes méthodes et de leurs résultats.
- Coordonner les activités des laboratoires, trop peu nombreux qui dans chaque pays essayent de conserver à l'Humanité les biens culturels qu'elle a hérité des siècles passés.

REUNION DU COMITE DE L'ICOM POUR LA CONSERVATION

Madrid , 2 - 7 octobre 1972

Technique de la restauration à la Bibliothèque Nationale de Jérusal

par Mme Esther ALKALAY

Chef du Département de Restauration

Bibliothèque Nationale
et Universitaire

Jérusalem

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TECHNIQUE DE LA RESTAURATION A LA BIBLIOTHEQUE NATIONALE DE JERUSALEM

L'absence de méthodes techniques dans le domaine de la restauration du papier a influencé les recherches et a fait naître des méthodes mécaniques de restauration.

Pour moi, l'idée m'est venue après la lecture d'un article de Nykeha dans lequel elle décrit comment elle travaille avec un appareil de restauration mécanique de laboratoire, semblable aux appareils utilisés dans les fabriques de papier.

Aujourd'hui, en Israël, à la Bibliothèque nationale et universitaire, nous avons construit le 5ème appareil perfectionné qui fonctionne avec succès, donne de bons résultats et répond aux besoins de la bibliothèque.

Quels sont la nature et le principe de la restauration mécanique à l'aide de pulpe de papier?

Il s'agit de fibres de papier finement broyés dans l'eau, qui s'infiltrent au travers d'un fin grillage, sur lequel reposent les feuilles à restaurer, et qui remplissent et s'accrochent uniquement aux trous, sans recouvrir aucune des surfaces imprimées.

Cette forme de restauration n'a pas seulement comme avantage de remplir les trous existants dans la page, mais renforce également le papier à tout endroit endommagé, et surtout à la jointure de l"ancien papier" avec le "nouveau papier".

Ce renforcement est fonction:

1) de la nature et de la qualité des fibres utilisés pour le remplissage des trous.

2) de la nature, de la qualité et de la quantité d'adhésif utilisé.

3) de l'exécution précise du processus de restauration, selon la nature des pages à restaurer, l'importance des dégats et la qualité du papier.

Il est évident qu'avant d'entreprendre le processus mécanique, les pages à restaurer doivent subir la même préparation que pour la restauration classique, c'est à dire:

- desinfection, (champignons, insectes divers, bactéries)
- notation et description sur fiche de l'état de l'objet à restaurer selon ses caracteristiques (après la restauration, nous notons sur la même fiche les travaux exécutes tant sur les feuillets que sur la reluire.)
- nettoyage à sec ou à l'aide d'un liquide selon les besoins - nous ne faisons jamais le blanchiement du papier.
- déacidification
- fixation de l'encre et renforcement du papier.

Une fois les pages preparées, elles sont agrafées par paire selon l'ordre des cahiers originaux.

Ensuite, les paires de feuillets sont reparties selon la forme et la surface des dommages (dans les manuscrits anciens, on trouve souvent plusieurs feuilles ayant subit les mêmes dégats).

Si le manuscrit comprend des pages dont le papier est de qualité différente, on classe les pages selon l'épaisseur du papier.

On pèse une page, 2 ou plusieurs et nous obtenons le poids moyen - $\underline{a}$ gramme - d'un feuillet. A l'aide de papier millimitré, nous calculons la surface de la page sans tenir compte des trous et nous obtenons - $\underline{n}cm^2$. Le poids d'$1cm^2$ sera $= Cgr = \frac{a}{n}gr$.

Le meme calcul peut se faire selon l'épaisseur du papier original quand nous le mesurons a l'aide d'un micrometre. La feuille que nous avons mesuré à l'aide du papier millimitré nous donne aussi la surface en cm^2 des trous, d'est à dire $\underline{d}$-cm^2 de trous.

Si nous voulons ajouter à chaque page des marges tout autour, nous devons ajouted au calcul gcm^2 qui serons les mêmes pour tous les feuillets.

Nous ajoutons ces marges parce que le pourtour de la feuille est toujours l'endroit le plus atteint, mais nous le faisons seulement sur des feuillets provenant de livres sans reliures originales, ou bien sur des feuillets d'archives.

Meme dans le cas de reluire originale, il est possible d'ajouter tout autour du feuillet, 1mm de marge. Ceci laisse neanmoins au chercheur la possibilite de voir exactement quelles etaient les dimensions precises de la page originale.

Maintenant nous avons les dcm^2 des trous qui sont les mêmes pour chaque groupe de feuillets et les gcm^2 des marges qui sont les mèmes pour tous les feuillets.

Nous additionons dcm^2 et gcm^2, que nous multiplions par Cgr et nous obtenons le poids de fibres sèches que nous devons ajouter pour combler les trous et les marges, et obtenir un papier nouveau de même épaisseur que l'ancien. Tous les feuillets sont maintenant classes et portent une etiquette sur laquelle figurent les dimensions nouvelles de la feuille (avec les marges et le poids de fibres en gr. à ajouter).

Nous utilisons de la cellulose sulfite blanchie ou non, et de la cellulose textile. Le melange de celluloses depend de la qualite du papier original.

La preparation des fibres se fait dans un "Hollender" dans une concentration de 2.5%, de 45° Shopper de la longueur moyenne des fibres. Une fois les fibres broyées, nous les mettons dans un grand seau à concentration de 12g par litre, environ. Afin qu'il n'y ait pas de difference de couleur dans les fibres utilisees, nous préparons une grande quantité de fibres, que nous teintons d'une couleur approchant l'original, selon les besoins et qui suffira a la reparation d'un livre entier.

Comme adhesif, nous utilisons le Polyvinile-Acetate, et la quan-

de la quantité d'eau que nous ajoutons dans la machine pour obtenir une émulsion homogène de fibres et de colle.

La surface de travail disponiqble du Recurator est 72cm x 52 cm. Nous recouvrons cette surface de soie naturelle, sur laquelle nous déposons les feuillets à réparer. Selon la grandeur des feuillets, nous pouvons déposer 1, 2, 4, 6 ou 8 feuilles doubles.

Nous baissons et fermons la partie superieure du Recurator, la remplissons d'eau, et lorsque celle-ci est a un niveau suffisant, nous ajoutons la pulpe et l'adhesif, selon les calculs préalables.

Nous melangeons parfaitement et activons le moteur. L'eau se retire et ne laisse que les fibres qui viennent combler les trous et les endroits manquants des feuillets.

Nous recouvrons les feuillets mouillés d'une gaze de soie naturelle. Les feuillets sont partiellement séchés entre des feuilles de buvard et ensuite nous mettons les feuillets nouvellement repares et enveloppes de soie dans un sechoir electrique.

Apres le sechage, nous coupons les feuilles à la grandeur desirée.

Le processus de restauration à l'aide du recurator ne depasse pas 3 minutes.

Dans les ateliers de Restauration organises et comprenant un personnel suffisant, on peut exploiter le Recurator dans sa capacite maximale, et ceci, en repartissant les diverses manipulations entre les membres de l'équipe. Le nombre de restaurations obtenues de cette facon est de loin superieur a toute autre forme de restauration.

Non seulement la quantité justifie la superiorite de cette forme de restauration mais aussi la qualite de la restauration elle-meme. Tout document aussi abimé, déchiré, réduit en morceaux, moisis, peut ici être restauré ou du moins, voir les morceux liés entre eux, sans que le texte ne soit couvert.

Aucune autre méthode, excepté la lamination, ne permet ceci. Dans ce cas precis, la lamination a pour defaut d'empecher au chercheur le contact direct avec le document et ceuxci sont alors presque perdus pour l'Histoire.

En toute responsabilité, et avec mon experience de restauratrice, longue d'une vingtaine d'années, je puis affirmer que cette methode de restauration ~~rejoint~~ répond au critères de bases de la restauration, qui sont:

1) la conservation et la restauration ne doivent en aucun cas changer l'originalité du document.

2) toute méthode de restauration doit permettre le retour en arrière, c'est-à-dire le retour à l'etat primitif du document.

3) les matériaux utilisés pour la restauration doivent rester sans influence, tant sur le papier que sur l'encre.

4) toute feuille restaurée ~~et~~ et soumise à un traitement de vieillissement doit "vieillir" moins vite que toute feuille non-restaurée.

Le Recurator permet également la préparation de feuilles neuves selon la qualité et la quantité désirés. Il est possible de faire figurer sur le papier tout filigramme desiré. Le papier nouveau ressemble à l'ancien papier fait main, et dont les bords sont irréguliers.

On peut faire une large utilisation de ce papier, soit dans les arts graphiques, soit en décoration. Les défauts de cette méthode de restauration sont:

1) surface limitée.

2) difficultés aves les manuscrits dont l'encre est impossible à fixer (en général des documents ecrits au style à bille ou avec de l'encre actuelle.

Tout ce qui vient d'être dit au sujet des manuscrits est valable également pour [illegible] documents imprimés

ICOM-Committee for Conservation - Madrid 1972

Dr. Adriaan Claerhout
Deputy keeper Archaeological Museums
Ethnographical Museum, Antwerp

ETHNOGRAPHICAL CONSERVATION AND THE MUSEUM CURATOR

1. Re-examination of the necessity of air conditioning for ethnographical collections in temperate zones.

Nobody among us needs to be convinced, neither of the fact that complete air conditioning creates the best conservation environment for objects of any kind, nor that financial investments for air conditioning equipment on long time save a lot of money on the restoration and personnel budget. There is however, as all of us know, a wide difference between this conviction from the scientific point of view, and the way of thingking of public authorities when confronted with the request of by all means impressive sums for air conditioning equipment, either in connection with plans for a new museum building or with plans for renovation of old quarters. Moreover, the same conviction may not keep us from re-examining the absolute necessity of air conditioning - the contrary would be very unscientific -, at least for museums in temperate zones, and certainly not refrain us from examining conditioning equipment other than the classic type.

By the way: I already discussed this problem with the specialists of the Brussels "Institut Royal du Patrimoine Artistique", and I am so to say convinced but do not completely feel sure.

In order to make clear, not so much my doubts as my needs for 100 % instead of 95 % argumentation, before myself in the first instance, of course also with regard to my authorities, I may put forward the following facts and questions.

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In order to make clear, not so much my doubts as my needs for 100 % instead of 95 % argumentation, before myself in the first instance, of course also with regard to my authorities, I may put forward the following facts and questions.

- Already several years ago, I was much impressed by an article by Mr. Günther Gall, published in "Museumskunde", 1960 and entitled : "Die klimatischen Bedingungen in Ganzglasvitrinen" (Climate conditions in all glass showcases) based upon experiments with showcases of "Glasbau Hahn, Frankfurt" in the "Deutsches Ledermuseum", Offenbach. These experiments surprisingly indicated that, even when abrupt changes of temperature and humidity were provoked in the museum rooms, conditions inside the showcases did not follow to the same extent. Indeed, temperature varied but 2° C - corresponding to 5° C in the museum rooms -, whileas RH never became lower than 52 % or higher than 55 % - corresponding to 22 % - 45 % in the museum rooms. Extended experiments led up to the conclusion that this type of showcases was so to speak self conditioning. Similar experiments were carried out with identic showcases in the Antwerp Folklore Museum, including cases with lighting units on top. It has there been observed that temperature maxima of 25° C and minima of 19° C in the museum rooms provoked temperature variations inside the showcases between 25° C maximum and 21° C minimum, which is after all fully acceptable; RH-measurement however was giving a maximum of 53 % and a minimum of 32 % in the museum rooms, inside the showcases maximum 47 %, minimum 37 % - whereas the ideal RH with regard to the temperature should have been between 45 % maximum and 40 % minimum; the result is thus less acceptable.

  It is obvious that the differences between the results in Offenbach and Antwerp are caused by different environment inside, perhaps also outside the building. But nevertheless it is demonstrated that a showcase fulfilling certain requirements regarding materials and construction can act as an air conditioner itself for at least a greater part, and that the conditions inside the showcase finally can be influenced by certain measures regarding the construction of the building. When supposing that this is not a false reasoning, I then must prefer a good building with good showcases without air conditioning system.

- In the meantime, I am conscious of the fact that it is not necessary to have the whole museum building air conditioned. Indeed, we just need to keep the objects in good condition, and so it is satisfactory to provide but the showcases with air conditioning equipment, which signifies already an important saving of investment and operation

costs. But then : what should we do with the storage rooms ? No problem here for lack of alternative : the whole room has to be conditione Not so with the temporary exhibit rooms, where usually one should be able to move the showcases. No air conditioning in this part would be in contradiction with the other parts of the museum. Conditioning the whole room, the storage rooms already conditioned, would mean a notable decrease of the savings intended.

- Last but not least a curious and current situation, especially in ethnographical museums, has to be mentioned: what's the good of air conditioning showcases, parts of the museum or even the whole museum building, when certain objects regularly have to be lent out and sent away under eventually the worst possible climate circumstances ?

My final question to the conservation specialists concerning this general conservation matter, with regard to the utmost heterogeneous collections of ethnographical museums may be as follows :

- Is full air conditioning, of either showcases or rooms, absolutely necessary, or at least highly desirable for museums also in temperate zones, and what are the most important reasons therefore ? In this case, the conclusions concerning what I might term the use of objects, have to be formulated as explicit as possible.

- If, always for museums in temperate zones, less rigorous measures should be satisfactory (e.g. air pollution control, effective pressure in the rooms or in the showcases, etc.), it would be very useful if these measures (including for construction of new buildings or adaptation of existing ones) could be formulated as simple as possible.

To this question I may add as footnote, that in the collections of the Ethnographical Museum of Antwerp(of which parts already existed about 1870, were exhibited in an old castle, afterwards removed to the attics of the Butcher's Hall, during the second world war transported to a 16th century warehouse, since twenty years stored in a partly 16th, partly 19th century mansion house) no serious damages have occured until now, except for lacquered wood sculpture, Asian furniture, and musical instruments. But I am fully aware of the fact that damages invisible for the moment may occur in the near future, and that for the future in general,

environmental conditions, especially in connection with air pollution, are to be feared.

The second topic of this paper is in connection with an other general problem in ethnographical museums, namely the storage of the different kinds of collections, not only from a practical point of view, but in the first instance from the conservation point of view, Recent experience leads me to present a

2. Proposal for efficient examination of storage systems.

Since a couple of years, a committee "Textiles - museums" is very active in the Netherlands. Thanks to personal relations I had the opportunity to participate in the meetings of this committee. During 1971 and the current year, attention was focused on presentation methods and storage systems of textiles in general.

Concerning the storage of flat textiles, a cheap provisory system presented by myself, was vehemently criticized by both textile engineers and textile conservation specialists, and I confess that their critics were largely convincing. My real problem however was to hear about or to see a storage system satisfying from the conservation point of view, and that at the same time could be realized with regard to the availability of the equipment proposed, preferably also with regard to financial possibilities Neither examples could be referred to, nor practical indications given. One textile engineer and one specialist in the conservation branch however apparently had been challenged by my question without answer, and this resulted, at the following meeting of the committee, in full information about kinds and availability of equipment accessories in complete agreement with both theoretical requirements and museological desiderata.

It is needless to underline that this was an utmost valuable result, in the first instance as a consequence of obstinately repeating the question, the more encouraging as it proves that our laboratory colleagues are indeed willing to help us also beyond their theoretical scope when we, museum keepers and curators, are asking for it.

However, the story I told you has to be followed by both a comment, and,

with your permission, the proposal announced.

It seems rather curious indeed, that the mentioned solution for an approximately ideal storage system for flat textiles has been found under the guidance of the eminent lecturer at Delft Technical University, Dr J.E. Leene, whereas in the recent book on "Textile Conservation", edited by the same Dr. Leene for I.I.C., London 1972, a similar but less satisfactory system is rather accidentally cited from the textile study collections of the University of Washington. This is by no means blaming the mentioned editor, but an exclusive illustration of what is resulting by lack of efficiently organized information. I therefore dare put forward the proposal to take the work of the Dutch Committee "Museums - Textiles", especially regarding the storage problem (the discussion of which started by mutual exchange of experiences) as an example for future work concerning storage systems of other kinds of objects - to mention but one of them : weapons. It seems to me not so complicated to compile information about various storage systems invented by various museum people all over the world - not only in ethnographical museums of course - , together with their own judgment based on personal experience. This should be followed by editing the information, which can be realized in an inexpensive manner. This information then should be sent for comments to both the museum colleagues who collaborated and the conservation specialists, say the members of the Committee for Conservation. Finally this should result in setting forward one or two preferable storage systems for each type of weapons, these results to be published as a handsome booklet.

This idea reminds me of another one, about which I talked with several leading persons in the conservation branch, who agreed but apparently neither judged it really necessary because of the existence of classic manuals on this subject, nor did they find the opportunity to pass on from wishful thinking ~~on~~ to concrete realisation. I would like now to attack the third topic of my talk, resulting in a

3. Proposal for a mini-handbook for conservation of ethnographical materials, (or perhaps not only ethnographical materials).

Be it understood that it is far from me to blame herewith our colleagues

in the conservation branch. All of us are fully aware of the intricate problems they have to deal with in their own institutions and countries, and of the lack of personnel they have to reckon with. In the meantime however, I am not sure at all whether, on the contrary, they are aware of our working conditions, especially in those institutions not having trained conservation personnel at their disposal. I am not sure whether they know that these museum colleagues just do not have the opportunity, neither to go systematically through the manuals for conservation nor to follow up the current literature in this field, published in a mass of periodicals belonging to divergent scientific branches - not to mention whether we are still able to understand the jargon of their explanations. May I take the liberty to extend the needs of especially medium and small sized ethnographical museums to the hundreds of so called folklore museums even to local museums of antiquities, for the reason that their collections in many respects are quite similar, claiming in the meantime that, if those museums are individually less significant, the patrimony of the total of them by no means can be neglected. As a matter of fact, I am partly repeating here what was already written by Stephan Gyermek (in "Museum News - Technical Supplement" - October 1964) as an introduction of what I might call an outline of principles and possibilities of Conservation of ethnographical collections.

Gyermek's technical note might well serve as an example of what is the subject of my proposal. While supposing namely, that Gyermek's outline is somewhat too limited, whereas it is obvious that some of the recommended conservation methods need rectification, I am thinking about a handbook for conservation exclusively intended for curators in medium and small size museums, and that therefore should not have the volume of a real manual, but should consist of a series of small chapters or booklets, each of them dealing with one kind of material, intelligibly written from the museum curator's point of view without going into details. As absurd as it may seem to be, the series should have to be introduced by a general remark concerning the various aspects of the necessity of conservation measures and treatments. Each chapter or booklet should mention in the first place the different general taboos; in the second place various general commands; thirdly an always concise survey of typical material deteriorations including preferably the least complicate treatments to apply - and indicating at which degree of deterioration

or damage intervention of trained persons is required -; fourthly and to end it a list of conservation materials adapted to each country or group of countries.

I feel the realisation should be in the hands of a working team of conservation specialists and museum curators, and I believe that, under the condition that the volume should be limited to what for this occasion I call a mini-handbook, all of the national ICOM-committees or groups of committees will be able to manage not only to get the original version translated and adapted, but last but not least to edit the handbook for the convenience of even the smallest collection - why not also private collections ? - in their country.

Perhaps the most essential objection conservation specialists will feel obliged to put forward against this proposal is, that the above drafted formula holds concrete risks in so far that a volume limitation implies limited explanations which may lead to uncomplete and thus false interpretations and treatments. I may submit to the judgment of the Committee for Conservation whether the risks balance the evident advantages.

I thank you for your kind attention.

Traitement des objets ethnographiques au laboratoire du Musée National des Arts et Traditions Populaires

(version provisoire)

G. Delcroix (Centre de Recherches Archéologiques)

F. Déon (Musée National des Arts et Traditions Populaires)

"L'organe de conservation" du Musée National des Arts et Traditions Populaires fonctionne depuis deux ans. Il s'étend actuellement sur une surface d'environ 200 m2 qui se répartit en cinq départements. Le traitement des objets comprend trois départements - matériaux poreux (essentiellement bois, céramique, pierre) matériaux métalliques, matériaux textiles et végétaux. La mise au point de traitements nouveaux et l'analyse des objets à des fins d'études technologiques mobilisent les deux autres départements.

Cet organe se définit comme "laboratoire technique". En effet le matériel dont il est équipé l'autorise à "procéder à des essais de microscopie, de microchimie et de physique ordinaire" et à tirer profit "d'un plus large éventail de méthodes de conservation et de restauration". Mais l'acquisition récente de nouvelles possibilités tant du point de vue analytique que du point de vue traitement lui donne une nouvelle vocation de "petit" laboratoire scientifique.

Au personnel permanent (deux ingénieurs, trois techniciens de la conservation) se joignent quelques étudiants de l'Université de Paris I qui y effectuent des stages de longue durée ou y préparent des diplômes de maîtrise.

Notre tâche est de traiter autant les objets ethnographiques des collections que les objets archéologiques provenant des fouilles associées au Musée.

roblèmes posés par le traitement des objets ethnographiques du Musée National des Arts et Traditions Populaires (1)

Les objets ethnographiques sont constitués de matériaux très divers. En plus des métériaux traités dans les laboratoires de conservation d'objets archéologiques, d'archives ou de peintures, nous trouvons des espèces nouvelles - végétaux séchés ou non, spécialités gastronomiques régionales, aluminium et plastique - qui soulèvent des problèmes spécifiques.

La communauté de matière n'entraîne pas ipso-facto le recours aux méthodes traditionnelles de traitement en particulier celles des objets archéologiques mais impose la création de méthodes adéquates.

En effet les produits d'altération sont différents. D'abord l'environnement naturel des objets n'est autre que l'atmosphère urbaine, rurale ou marine, excepté pour les objets agricoles qui sont parfois plus corrodés de par leur contact avec les matières humiques (fumier....). En outre le paramètre temps n'a pas suffisamment joué pour que les transformations d'ordre chimique, électrochimique, biologique ou mécanique aient atteint le terme de leur évolution. C'est pourquoi l'altération de type uniforme constituée de produits d'altérations simples est la plus fréquente et par là même nous rapproche des problèmes de traitement de surface de l'Industrie. Il est bien rare que les objets ethnographiques soient des unicas. Ils se présentent plutôt sous forme de séries d'une dizaine ou d'une centaine d'éléments, ce qui implique un traitement de masse.

Cette notion de traitement de masse tient compte aussi de la valeur commerciale de nos objets, peu onéreux dans l'ensemble. En aucun cas le prix du traitement ne doit dépasser cette valeur. Cette préoccupation de rentabilité qui certes joue peu dans les autres domaines de la conservation est comparable à celle du monde industriel.

Il existe néanmoins quelques obstacles au traitement de masse. Les objets ethnographiques sont essentiellement composités, démontables ou non. Si l'objet est démonté et chaque partie constitutive traitée séparément, l'arbitraire de la

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(1) Les idées exprimées ici reviennent en très grande partie à G.H. Rivière et sont le reflet de l'expérience de la galerie d'études: 5.000 objets traités.

restitution du montage primitif est un grave danger. La solution du second cas nous est encore inconnue.
Enfin n'oublions pas que leur grande taille est encore un handicap.

L'aspect final de l'objet est une autre question importante à débattre. Nous rendons à l'objet la "patine d'utilisation" à condition que celle-ci ne soit pas contradictoire avec la conservation de ce dernier. Nous refusons toute "restauration du type pseudo ethnographique" et laissons l'objet dans un état de fonctionnement apparent.

Afin d'éclairer nos démarches, nous avons consulté une bibliographie spécialisée d'une indigence regrettable. C'est pourquoi nous proposons quelques réflexions sur les problèmes de nettoyage, de consolidation, de restauration et de conservation.

Réflexions sur les problèmes de nettoyage.

Il existe 4 types de méthodes de nettoyage - mécanique, thermique électrolytique ou électrochimique, chimique.

La méthode mécanique utilise des procédés par piquetage (statique ou dynamique), par frottement, par vibration à basse ou haute fréquence.

Nous expérimentons un procédé par piquetage connu industriellement sous le nom de "vapor blast" (1). Des matériaux abrasifs sont projetés par l'intermédiaire d'un support liquide. Cet appareil nous offre une gamme de manipulation plus large puisque les effets de l'abrasif et du liquide ainsi que leur concentration relative se conjuguent.

Nous avons retenu comme procédé de vibration à basse fréquence le burin de graveur. Il permet de retirer ponctuellement les produits d'altération enchassés dans la matière. Son emploi n'est cependant recommandable que dans le cas d'un objet parfaitement sain, c'est-à-dire sans fissure.

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(1) méthode signalée par Plenderleith et Torraca dans la préservation des biens culturels mais uniquement pour les métaux . Son emploi s'avère beaucoup plus large.

Le procédé par vibration à haute fréquence - ultra-sons - n'est employé qu'à titre expérimental. Nous ne possédons en effet qu'une cuve de petites dimensions. Ce type de nettoyage est d'une efficacité incontestable pour les textiles et pour le dégraissage des métaux avant traitement chimique.

Il va sans dire que le traitement mécanique est de faible rentabilité, et que les parties cachées des objets composites demeurent inaccessibles.

La méthode thermique supprime les couches d'oxydes grâce à la différence de coefficient de dilatation avec le métal de base. Les poussières organiques ou les résidus de graisse introduits par la manipulation manuelle sont aussi éliminés. Nous avons rejeté cette méthode pour les raisons suivantes :

- sécurité non garantie
- prix de revient élevé
- ignorance en ce qui concerne les modifications éventuelles de surface ou le gauchissement des pièces.

La méthode electrolytique n'a été appliquée qu'à deux types d'objets : métalliques, composites métal-bois, après dégraissage préliminaire. Dans le premier cas, la méthode convient parfaitement car nos objets possèdent un coprs métallique important et des produits de corrosion peu adhérents. Au montage cathodique qui comporte un risque de fixation d'hydrogène, nous avons préféré un montage alterné. Le nettoyage des emplacements cachés n'est pas encore satisfaisant. Le procédé "Bullard Dunn" résoud le problème dans le cas des objets de fer. Ceux-ci sont immergés dans une solution acide contenant de faibles quantités d'étain. Dès l'apparition du "métal à nu" la première couche d'étain se dépose. Par suite de la surtension de l'hydrogène sur l'étain le courant est dévié vers les autres points non encore nettoyés.

Quelque soit le procédé employé l'electrolyte ne doit pas contenir d'ions Cl - qui dans le cas d'un rinçage défectueux risqueraient de provoquer une corrosion ultérieure par piqûres. Les opérations ne seront donc conduites qu'avec des "produits purs".

Nous avons aussi employé l'électrolyse pour traiter des outils indémontables. Bien que lent, le traitement electrolytique s'est montré plus efficace que le traitement mécanique car il atteint tout de même mieux les parties cachées.

Nous avons concentré notre intérêt sur les méthodes chimiques de nettoyage, les métaux ayant la première place.
Tous nos essais comportaient

1 solvant organique des graisses

1 constituant acide

1 composé tensio actif favorisant le mouillage de la surface et destiné à émulsionner les graisses.

1 modérateur d'attaque

1 produit mouillant pour faciliter la pénétration du mélange dans les emplacements cachés.

De l'eau comme solvant.

Ces méthodes sont peu onéreuses. Elles permettent le traitement de masse, mais le cas des objets composites n'est pas réglé pour autant excepté pour l'association de plusieurs métaux.

Quelque soit le type de nettoyage, en fin de traitement se posent trois problèmes : rinçage et neutralisation de l'objet
séchage
polissage.

De la qualité du rinçage dépendra l'évolution de l'objet. Nous introduisons actuellement pour faciliter le rinçage un agent de mouillage et une agitation par air comprimé.

Le développement de l'automation des processus de nettoyage des objets ethnographiques nous invite à employer les techniques de rinçage de l'industrie. L'évacuation de l'eau est commandée par une valve magnétique contrôlée par une cellule de conductivité réglée sur une pureté déterminée (spécification encore à définir pour nos problèmes).

Le séchage n'est jamais parfait. La sciure de bois, l'étuve favorisant le dépôt de produits générateurs de corrosion. La technique sous vide constitue sans aucun doute le moyen idéal mais faut-il encore avoir une cuve de dimensions adaptées à celles des objets. C'est pourquoi nous mettons au point deux types de traitements chimiques :

- le premier emploie des mélanges à chaud et parfaitement anhydres
- le second un solvant non aqueux.

Quant au polissage, il est effectué avec un touret. Une solution à la lenteur de l'opération pourraît être le polissage electrolytique ou chimique.

Réflexions sur les problèmes de consolidation (1)

La consolidation des métaux se fait par soudure à froid

La consolidation des matériaux poreux (bois, pierre, gâteau...) est réalisée par imprégnation sous vide avec des résines métacryliques pour la plupart. Comme la profondeur d'imprégnation est insuffisante, nous faisons alterner uns phase sous pression avec une phase sous vide. L'autre avantage de ce procédé est l'imprégnation des micropores.

Notre intention est de généraliser ce dernier procédé pour les objets métalliques et d'étendre l'emploi d'inhibiteurs aux objets non métalliques.

L'élaboration d'un programme de recherches est la conséquence de nos préoccupations. Quelle peut être sa relation avec le programme plus général de la section ethnographique de l' I.C.O.M ?

Notre programme s'articule en 2 volets : un volet bibliographique et un volet expérimental.

Le volet bibliographique comprend trois parties. Les deux premières sont en cours d'achèvement.

- méthodes domestiques de nettoyage et d'entretien
- méthodes industrielles de nettoyage
- enquête photographique sur le problème de la patine d'utilisation.

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(1) Les solutions pour le textile sont celles du laboratoire de la fondation Abbey à Riggisbery.

Le volet expérimental comprend :

- amélioration des méthodes de nettoyage chimique en phase liquide (anhydre et solvant non aqueux), en phase gazeuse.
- amélioration des méthodes de consolidation par une étude approfondie des divers paramètres
- amélioration des méthodes de conservation par l'emploi d'inhibiteurs de corrosion
- problèmes du polissage électrolytique.

Cette présentation des recherches du laboratoire d'analyse et de restauration du Musée National des Arts et Traditions Populaires ne saurait être complète si l'on ne mentionnait pas les moyens de diffusion de nos recherches :

. Enseignement à l'Université de Paris I : Institut d'Art et d'Archéologie. Cet enseignement est consacré dans une large mesure au traitement des objets archéologiques (1).

. Publications dans le cadre des "notes et monographies du Centre de Recherches Archéologiques" dans la revue d'ethnologie française.

. Distribution de "notes techniques" à partir du mois de Novembre sur les méthodes de traitement appliquées dans notre laboratoire et à usage des techniciens de conservation. (voir Annexe I ..)

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(1) Un polycopié de l'enseignement donné sera distribué aux étudiants pour l'année 1972-1973.

Traitement des objets ethnographiques en fer

G. DELCROIX (C.R.A.)
G..GENIN (I.R.P.A.)

I - Introduction

Le laboratoire du Musée National des Arts et Traditions Populaires utilise pour le traitement de masse des objets ethnographiques en fer un dérouillant à base d'acide orthophosphorique. Le traitement sur 2.500 pièces nous a permis de cerner une méthode exploitable par tout atelier de restauration. Il s'adresse à 3 catégories d'objets :

- objets en fer
- objets bois + fer démontable
- objets bois + fer non démontable

étant entendu que le mot fer englobe l'acier et la fonte. Ces objets se présentent "rouillés" de façon uniforme ou par piqûres mais avec un corps métallique très important.

II - Méthode de traitement

1. équipement nécessaire

- 1 bac en matière plastique
- 3 bacs en métal, adaptés à la plus grande dimension des objets à traiter
- 1 touret mécanique 3000 t/mm réglable équipé de brosses circulaires à fils d'acier. La dimension des brosses est en relation directe avec la rapidité et l'efficacité du traitement mécanique
- 1 réchaud électrique
- brosses métalliques à main à fils d'acier mi-dur

2. produits nécessaires

- acide orthophosphorique vendu commercialement sous le nom de déoxidine 670

- alcool étylique
- benzoate de soude
- cire cosmolloïd et cire d'abeille
- huile de vidange ou pétrole
- noir de fumée
- trichloréthylène

III - Technique opératoire

1. Objets en fer

Ces objets sont traités comme suit :

- nettoyage à l'aide d'une solution aqueuse chaude de benzoate de soude à 1% pour éliminer les salissures non grasses.
- dégraissage au trichloréthylène pour éliminer les graisses qui empêcheraient un bon contact fer-produit dérouillant; le trichloréthylène étant un produit toxique, il est recommandé d'opérer avec une ventilation efficace.
- immersion dans un bain aqueux de déoxidine à 30 % pour dérouiller. L'opération peut se faire à froid mais une température de 50° obtenue par l'intermédiaire d'une source infra-rouge plongeante accroît l'activité du produit.
- brossage à l'aide de la brosse à main et sous eau courante.
- séchage au chiffon puis à l'alcool.
- polissage mécanique
- répétition de l'immersion dans un bain de déodoxine si nécessaire
- dégraissage au trichloréthylène
- immersion dans un bain d'huile de vidange ou de pétrole
- imprégnation à chaud de cire noircie au noir de fumée avec un peu de benzoate de soude.

- alcool étylique
- benzoate de soude
- cire cosmolloïd et cire d'abeille
- huile de vidange ou pétrole
- noir de fumée
- trichloréthylène

III - Technique opératoire

1. Objets en fer

Ces objets sont traités comme suit :

- nettoyage à l'aide d'une solution aqueuse chaude de benzoate de soude à 1% pour éliminer les salissures non grasses.
- dégraissage au trichloréthylène pour éliminer les graisses qui empêcheraient un bon contact fer-produit dérouillant; le trichloréthylène étant un produit toxique, il est recommandé d'opérer avec une ventilation efficace.
- immersion dans un bain aqueux de déoxidine à 30 % pour dérouiller. L'opération peut se faire à froid mais une température de 50° obtenue par l'intermédiaire d'une source infra-rouge plongeante accroît l'activité du produit.
- brossage à l'aide de la brosse à main et sous eau courante.
- séchage au chiffon puis à l'alcool.
- polissage mécanique
- répétition de l'immersion dans un bain de déodoxine si nécessaire
- dégraissage au trichloréthylène
- immersion dans un bain d'huile de vidange ou de pétrole
- imprégnation à chaud de cire noircie au noir de fumée avec un peu de benzoate de soude.

2. Objets bois + fer démontable

Le traitement se ramène au traitement des objets de fer.

3. Objets bois + fer non démontable

Le traitement s'effectue par immersion de la partie métallique de la pièce dans le dérouillant : la protection du bois des vapeurs d'acide phosphorique est assurée par un revêtement étanche de cire d'abeille. L'imprégnation de conservation se fait au pinceau après chauffage préalable du métal.

The International Council of Museums
Committee for Conservation

Conseil International des Musées
Comité pour la Conservation

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Virginia Greene, University Museum, Philadelphia.

THE USE OF BENZOTRIAZOLE IN CONSERVATION: PROBLEMS AND EXPERIMENTS

In the course of ten years of commercial use benzotriazole has proven to be a remarkably effective and versatile corrosion-inhibitor for copper and copper alloys. The possibility of using it for the conservation of antiquities was first brought to the attention of conservators in 1967. The reported success of the treatment was so startling that it seemed to provide, at last, a satisfactory answer to the problem of permanent and effective stabilization of objects without the removal of corrosion products. Since that time, benzotriazole has been used by many conservation departments, but with inconsistent results. Madsen, who originally proposed the treatment, has never stated by what process he arrived at the procedures that he recommends, nor has there been any attempt to set up a program of systematic testing to establish the limits of effectiveness of benzotriazole when used under laboratory rather than industrial conditions, or to determine the most satisfactory method(s) of treatment.

Although a large-scale project of this kind would require the facilities of a research laboratory, it seemed that a certain amount of useful information about benzotriazole could be obtained by means of simple tests which could be carried out with a minimum of equipment. In the course of preliminary library research it also became apparent that Madsen's original discussion of the chemistry of the compound was inadequate and misleading, and that

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a clear picture of the chemical properties of benzotriazole was an essential prerequisite to any consideration of its use in conservation. The results of this research are too extensive for inclusion here; only the aspects most directly connected with the experimental work will be summarized. It should be noted that all of this information is the outcome of industrial research concerned with the prevention of corrosion on clean, recently-fabricated metal surfaces.

I.

The protective films formed by the action of benzotriazole (BTA) on copper were measured and found to be less than 50Å thick. It proved impossible to study the chemistry of the bonding directly on the metal and it was decided to produce the copper-BTA complexes by precipitation in aqueous solution in order to obtain sufficient material for study (Cotton and Scholes, p.l.). This is of particular interest to conservators as it involves possible reaction of BTA with corrosion products as well as with exposed metal surfaces.

This approach, however, has created the additional problem of justifying the identification of the precipitate produced in solution with the film formed on the metal, though there are reasonable arguments for assuming at least a close similarity. Only the compounds which form insoluble precipitates offer any protection to metal surfaces, and the fact that the surface films cannot be removed by washing (with water or organic solvents) suggests that a true chemical bond is involved, similar to that observed when precipitates are formed in solution. (Cotton and Scholes, p.1,3).

The results of the most recent chemical and physical analyses of the precipitates are summarized as follows:

COMPOSITION OF CUPROUS AND CUPRIC BTA COMPLEXES

(ADAPTED FROM COTTON AND SCHOLES 1967, TABLE I)

	CUPROUS DERIVATIVE			CUPRIC DERIVATIVES				
	ORIGINAL THEORY $BTA \cdot Cu$	(1) FOUND	PROPOSED FORMULA $(BTA \cdot Cu)_9 \cdot 2H_2O$	ORIGINAL THEORY $(BTA)_2 \cdot Cu$	(3) FOUND WITH $CuCl_2$	PROPOSED FORMULA $[(BTA)_2Cu]_2CuCl_2 \cdot H_2O$	(2) FOUND WITH $CuSO_4$	PROPOSED FORMULA $[(BTA)_2Cu]_3 \cdot 2H_2O$
C	39.7%	39.7%	39.0%	48.1%	38.7%	38.4%	45.9%	46.3%
H	2.2	2.4	2.4	2.7	2.6	2.4	2.9	3.0
N	23.1	22.5	22.7	28.0	23.3	22.4	26.5	26.9
Cu	35.0	33.7	34.1	21.2	25.5	25.4	21.2	20.4
O	—	1.9	1.9	—	2.4	2.1	3.3	3.4
Cl	—	—	—	—	9.9	9.3	—	—

(1) Amorphous or microcrystalline.

(2) Amorphous or microcrystalline. According to Cotton and Scholes (p.3), "not a normal cupric derivative", but this statement is not explained.

(3) Crystalline. The crystalline structure and the proportions of copper and chlorine present suggest that they are present as molecules of cupric chloride, but this has not been proven (Cotton and Scholes, p.3).

The cupric chloride derivative analyzed apparently is formed only when the reaction takes place in the presence of excess cupric chloride. It is not at all clear what happens under other circumstances, but this peculiarity in the reaction of cupric chloride with BTA raised the possibility that the presence of chlorides might have a distinct and determinable effect on the nature of the precipitate formed. This was also suggested by the data obtained from x-ray diffraction examination of metal surfaces treated with BTA.

If a clean copper surface is treated with pure aqueous BTA, the crystalline film of cuprous oxide normally present is replaced by a film which is amorphous or microcrystalline. The composition of the latter is apparently similar to the cuprous BTA derivative precipitated in solution (Prall and Shreir, p.253). If the film is formed in the presence of chloride, however (potassium chloride as well as cupric chloride were added to pure aqueous BTA), it is crystalline, and gives an x-ray diffraction pattern similar to that of the complex precipitated with cupric chloride in solution (Cotton, p.592; Cotton and Scholes, p.3). It is not known whether this would also be the case if the film were formed in the presence of cuprous chloride. No attempt has been made to explain the relationship of all this to the reaction observed with copper sulfate in solution, nor does there seem to be any functional difference between the two films described above: both appear equally protective.

II.

In his article, Madsen gives the following procedure for the treatment of antiquities (Madsen, p.164): Loose dirt and corrosion are removed with a glass-bristle brush, the object is degreased with a mixture of acetone and toluene, and then immersed in a 3% solution of BTA in alcohol (industrial methylated spirit) under vacuum, until bubbles are no longer visible. Madsen notes that water can also be used as a solvent, but that BTA is less soluble in water, and the higher surface tension will hamper

impregnation. He does not, however, give any reason for his choice of a 3% solution -- the fact that BTA is less soluble in water is not relevant unless it can be demonstrated that a 1% solution is less effective in treating antiquities than a 3% solution. Moreover, Madsen goes on to say that if a vacuum pump is not available, the object can be immersed in a 3% solution of BTA in water at 60°C. One would imagine that if water is unsuitable as a solvent for treatment under vacuum, it would be even less suitable for immersion without vacuum. Madsen does not give any suggested duration for the latter treatment, or make it clear why he has chosen a heated solution rather than one at room temperature.

Another potential problem has also become apparent. All of our information on the composition and behavior of BTA precipitates and surface films refers to complexes formed in aqueous solution, rather than the alcohol solution porposed by Madsen as a standard treatment for antiquities. It is possible to protect an antiquity as well as a clean metal surface in either solution, but there is no evidence that the reaction with copper salts are identical.

All three precipitates formed in aqueous solution include extra atoms of oxygen and hydrogen, at least some present as bonded molecules of water and the rest either as water or hydroxyl groups (Cotton and Scholes, p.3). Cotton and Scholes suggest that these extra molecules play a part in stabilizing the copper-BTA complexes, i.e., that the bonded water may be essential to ensure the long-term protective effect of the surface films.

If one accepts this, even as a hypothesis, it seems worthwhile to consider the possibility that precipitates and surface films formed in methylated spirits, with a water content of only 2-3%, might differ from those formed in aqueous solutions, not only in composition but in their ability to protect antiquities.

It may be noted that although BTA is used commercially in ethylene glycol solutions, in these cases a permanent reservoir of BTA is in contact with the metal (Desai, et. al., p.19); moreover, the solution usually also contains the needed water. As far as I know, all industrial treatments for atmospheric inhibition use aqueous solutions.

III.

Qualitative analysis of precipitates or examination of surface films with special equipment was beyond the scope of this project, but a series of simple comparative experiments was carried out in an attempt to obtain basic information about the behavior of BTA under normal laboratory (as opposed to industrial) conditions.

(1) Immersion tests on copper blanks, using BTA in alcohol solutions, to determine whether a concentration lower than 3% would protect antiquities, and what duration of treatment was necessary. These questions related directly to Madsen's recommended procedure.

(2) Immersion tests on copper and bronze blanks to determine whether the presence of amphoteric metals had an effect on the action of BTA. This problem was the result of a series of unsuccessful treatments at the Institute of Archaeology, London.

(3) The formation of BTA precipitates in aqueous and alcohol solutions, to establish any visible differences in the reactions or in the appearance of the precipitates.

(4) Immersion tests on copper blanks, using BTA in both aqueous and alcohol solutions of varying concentrations.

(5) Immersion tests on copper blanks, using BTA in aqueous solutions at varying concentrations and temperatures.

The results of this work will be presented at the meeting, with suggestions for future research.

WORKS CITED

Cotton, J.B.
1963 Control of Surface Reactions on Copper by means of Organic Reagents. Proceedings Second International Congress on Metallic Corrosion, New York.

Cotton, J.B. and I.R. Scholes
1967 Benzotriazole and Related Compounds as Corrosion Inhibitors for Copper. British Corrosion Journal, vol.2, no.1, pp.1-5.

Desai, M.N., S.S. Rana and M.H. Gandhi
1970 Corrosion Inhibitors for Copper. Anti-Corrosion Methods and Materials, vol.17, no.6, pp.17-21.

Madsen, H. Brinch
1967 A preliminary Note on the Use of Benzotriazole for Stabilizing Bronze Objects. Studies in Conservation, vol.12, no.4, pp.163-167.

Prall, J.K. and L.L. Shreir
1965 A Study of Benzotriazole as an Addition Agent for Acid Copper Sulphate Solutions. Transactions of the International Institute for Metal Finishing, vol.42, pp.246-257.

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Hanna Jedrzejewska

ANALYTICAL PROBLEMS IN A MUSEUM LABORATORY

(non-ferrous metal artifacts)

This report follows a Questionnaire prepared by me under the title "Simple methods of analysing non-ferrous metals in museums" and sent out by the ICOM Committee for Conservation in 1969 to various specialists in the study of metal antiquities. Several replies to this questionnaire expressed interest in participating in further work on the problem. For reasons not under my control I was not able to participate in the 1969 ICOM Meeting in Amsterdam and it is only now that I can proceed with this project.

General considerations

There is no need to discuss the importance of the chemical study of ancient artifacts. But there is a question of how much of this kind of study can be done and by what means. The purpose of the data obtained will depend not only on the particular intentions and the means available, but also on the kind of problem investigated and the state of the artifact.

The purpose of the chemical study is to gain information on the composition of materials in artifacts. This may be done in order to:

(1) collect information that has a direct bearing on the choice of method of treatment. For example, the presence of gold or other surface coating under layers of corrosion, or the presence of certain metals in alloys, etc., may make certain kinds of treatment impossible.

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(2) preserve information on materials that will be lost or destroyed during treatment. For example, this concerns all accumulations on the original surface, as well as changes to the surface itself when chemical or electrochemical methods of cleaning are applied (leaching out of some components, deposition of foreign elements, chemical transformations, etc.).

(3) collect information not directly connected with the treatment. In this case the information of interest will not be lost but at the time of treatment the contact with the object is particularly close and gives the best opportunity for taking all kinds of samples. This kind of chemical study is needed for historical and technological purposes (authentication, method of fabrication, dating provenance, etc.).

In cases (1) and (2) the analytical information is needed immediately, though in case (2) the samples can be collected for chemical study in the future. Also, when the object is cleaned by mechanical means only, a fragment of uncleaned surface can be left as evidence for analyses to be made later. In case (3) the analyses are not necessary actually during the treatment as they will not be influencing the method of treatment.

The scope of the analytical examination will depend on the purpose of the test as well as on the artifact itself. In cases (1) and (2) only some particular fragment of information may be needed. In case (3) it is expected to have all available evidence, accurate and complete, collected in the course of analytical examinations.

Depending on the purpose and scope of the chemical study of the artifact, different analytical procedures will be used:

- the fewest problems will arise from qualitative analyses, where only the identification of particular components is necessary. There are many methods available here and a large amount of published information. The most commonly applied tests are spot (colour) and microcrystalline tests. Several physical methods, also of the non-destructive kind, are well adapted for this purpose too.

- for quantitative determinations either large samples are required for conventional wet analyses or very small samples are examined by instrumental physical and physico-chemical methods. These latter procedures need highly accurate instruments and a specialised staff and are both very expensive and time consuming. But the highest accuracy in analytical data is justified only in the case of samples taken from very homogeneous materials (which are rarely found): it would be useless and extremely misleading to collect analytical data of great accuracy in the case of samples taken from highly heterogeneous materials, for example, a strongly corroded alloy). In most cases there is neither the need nor the possibility of really getting information of such accuracy.

Thus, when information is needed on the approximate proportions of principal constituents, or on a problem of similar calibre, there may be no real need for elaborate quantitative determinations.

In this event, semi-quantitative determinations are all that is needed. Instrumental equipment may be a great help here, not because of its high accuracy and precision, but because it ensures ease and speed of manipulation. An instrument makes things simpler, but in fact any semi-quantitative method could be used here, especially if it were quick and simple.

Depending on the kind of analytical work that has to be done and the available facilities, the analyses can either be carried out directly in the museum laboratory or samples can be sent to highly specialised research laboratories. In the case of only qualitative identifications, directly relevant to problems of treatment, the tests can usually be done directly in the museum laboratory. They are reasonably easy and do not take much time if a proper analytical kit is held in working readiness. The number of these analyses is rather large and their supply is continuous and the results are often needed almost immediately. On the other hand, quantitative determinations of great precision can be made only on special instruments by well-trained personnel. Such facilities are only very seldom included in the program of a museum laboratory, so samples have to be sent to other specialised institutions. This greatly reduces the number of samples that

can be analysed (for financial reasons) and only a limited number of artifacts can benefit from such facilities. There is also usually a long period of waiting for the results.

In most cases, semi-quantitative analyses could provide most of the currently needed information. And this, as already mentioned, could be carried out in the museum laboratory, provided that methods could be worked out not needing instrumental equipment. Such a possibility could indeed solve many of the present analytical difficulties suffered by museum laboratories. It could also help in enlarging the field of chemical research into artifacts.

Problems in semi-quantitative analytical procedures

Before any methods of testing can be suggested it is first necessary to consider the basic problems of sampling, the methods of dissolving the sample to make the test solution, and the way in which the collected data will be presented. Also the availability of reagents and the ease of the testing procedures have to be taken into account.

The sample. The problem of the correctness of the sample is often overlooked or generalized. Often, just "a sample" is being analysed. Nothing could be worse. The significance of the sample and how representative it is have to be clearly stated and proof given of their accuracy if the analytical data are to have any meaning at all.

The method of sampling. There are different methods of sampling, depending on the object, on the purpose of examination and on the method of examination. Samples can be removed from the interior or from the surface. Analyses can also be done on the object directly without removing any samples at all. For semi-quantitative determination a sample will have to be removed from the object. It may be very small but ideally it has to contain all components in their original proportion. In consequence it has to be removed as a solid fragment and not as a solution prepared directly on the surface of the object. In

this last case some preferential dissolution may take place, or some uncontrollable losses may occur during the collection of this solution for further analytical treatment.

The position from which the sample is taken has a direct bearing on its significance and representative qualities. Also, the size of the sample is of importance. The smaller the sample, the less representative it is compared with the bulk of the material.

Dissolution of the sample. For semi-quantitative analyses the whole of the sample fragment has to be dissolved at once. All components have to be in the same solution. This may present difficulties sometimes, especially when tin and lead (or silver) are present. The reagents for dissolution have also to be chosen so that they will not interfere with the tests planned.

Presentation of the collected data. Usually the composition of a sample is expressed in percentages. But this can only be done when the samples are weighed before dissolution. If the sample is too small for weighing, or if there is no analytical microbalance at the museum laboratory, the amounts of the particular components of the sample can only be expressed in terms of mutual proportions (for example, as 2:1 or 9:2, etc.) with a clear explanation of the meaning of these figures and how they were calculated. There seems at present to be a certain lack of uniformity in presenting the data from chemical analyses. Sometimes these figures represent the amounts of particular elements, sometimes of oxides, and sometimes even of the original compounds. The same concerns percentage evaluations. In many cases they seem not to be correlated with the weight of the sample and the possible presence of minor constituents is not accounted for.

Availability of reagents. This also is a factor that has to be considered as having influence on the choice of analytical procedure. If a testing method is to find wide application, especially in museum laboratories with modest funds and limited availability of supplies, the reagents have to be of an easily available kind.

The testing procedure. Depending on the available facilities, different testing procedures can be used. The semi-quantitative methods for museum laboratories have to be simple, easy, quick, inexpensive, reliable. No elaborate equipment should be necessary. The only necessary condition will be that the person doing the analyses should be well trained for this kind of work.

The "ideal" semi-quantitative method for use in museum laboratories should therefore satisfy the following requirements:

(1) give the right level of accuracy.

(2) give a possibility of allowing separate tests for the individual cations when starting from the same solution.

(3) be if possible direct, without multiple procedures for the test solution, as this might cause losses of analysed material.

(4) the individual tests should be specific for each particular cation, with no interference from other cations present in the solution.

(5) the tests should be able to indicate differences in the concentration of the cation tested.

(6) the tests should not be too sensitive to conditions of testing (pH, concentration of reagents, proportions of reagents).

(7) the evaluation of results should be quick and easy, preferably based on standard solutions of similar composition.

(8) the technique of testing and the sensitivity of tests should be adaptable to analyses of very small samples.

If a method could be found filling all of these requirements it would be extremely welcome in museum laboratories. The semi-quantitative analytical methods presently available are not applicable here. In most cases they are composed of several operations and are easily disturbed by the presence of different components.

The theoretically possible simple testing procedure.

As one of the theoretical possibilities qualitative spot-tests could be adapted to semi-quantitative determinations. Well-chosen colour reactions performed under strictly controlled conditions could well serve to indicate the concentration of the cation analysed. The colour obtained with the cation in the test solution could be compared with colours obtained with the same cation from standard solutions of known concentrations, and from this the approximate concentration of the cation in the test solution could be evaluated. This could be done easily if all of the testing were carried out within areas of exactly the same size and with the same amount of solutions.

The confined-area tests. This idea was used in the "Yagoda confined-area spot-test papers" (Carl Schleicher and Schuell Co, USA) with the reaction area = 100 sq. mm. Quite independently of this, the present author started working with small circles ("confetti") of thin filter paper impregnated with the right reagent. These circles were cut out from a previously impregnated sheet of filter paper. A hole-puncher for paper was used for cutting the circles.

Micro-pipettes of the right volume (10 gamma) gave just the right amount of liquid to have the circles evenly soaked in solution without any excess flowing out. Several circles were impregnated with the reagent solution and standard solutions of different concentrations and the test circle was then placed next to the standard circle of most similar colour intensity. Such a test can be made in two steps: first, wide-range, to find the approximate concentration of the unknown; second, within a narrow range to have more accurate estimations. If this were to be done from the same initial solution, for all of the particular cations, on circles of the same size and with the same amounts of solution for each test, then the mutual proportions of particular cations in the test solution would be easy to calculate. With all equipment ready for use and with a certain amount of practice on standards the whole operation would not take more than a few minutes.

The equipment necessary is as follows: small bottles or beakers for the different solutions, a good supply of circles containing different reagents, a convenient number of micro-pipettes, distilled water, and reagents for preparing the solutions. A sufficient number of microscope slides and a good standard illumination would be almost all that might be needed for the suggested semi-quantitative method of colorimetric spot determination.

The course of analysis.

(1) A truly representative sample is dissolved in its proper solvent*. No weighing or other measurement is needed.

(2) From this solution drops of a standard size are put on restricted-area spot-test papers ("circles"), separately for each cation. The size of the drops is of no importance, provided that for all of the particular determinations with both the unknown solutions and the standards the drops are of the same size.

(3) The colours obtained with the unknown are compared with the colours obtained with standard solutions of different concentrations. The best match is selected.

(4) In this way the concentrations of the particular cations, as well as their mutual proportions, are evaluated for the amount of solution = one drop. This can be extended automatically to the whole sample - and to the bronze - within limits determined by the representative qualities of the sample.

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*Ch. M. Dozinell. Modern Methods of Analysis of Copper and its Alloys. Elsevier. 1963, pp. 76 - 78.

The purpose of the present report.

The purpose of this paper is, first of all, to draw attention to the possibility of making analytical problems in museum laboratories easier than they are at present. Secondly, to attract a group of active collaborators to look for promising reagents, to suggest other possible procedures and eventually to write detailed instructions about the proper standardized ways of carrying out the determinations. This kind of work could be useful not only for problems of metals but also for many other analytical problems in a museum laboratory.

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M. Kalish, WCNILKR, Moscow.

EXAMINATION OF THE PROTECTIVE PROPERTIES OF THE NATURAL ATMOSPHERIC PATINA OF BRONZE MONUMENTS

The specific feature of traditional artistic tin bronzes is their ability to develop natural patina while exposed out-of-doors. This patina is very highly appreciated due to its well known decorative properties. Its physico-chemical characteristics, that determine quality of a patina as a protective film, are less known. But to evaluate the natural patina properly and to compare artificial decorative-protective coatings with natural ones it is necessary to know these characteristics. With this aim, samples of patina of different kinds were evaluated by appropriate standardized tests. It was done by methods used in the laboratory to examine coatings on copper and its alloys.

The natural patina is a deposit of copper corrosion products which has different composition and structure depending on age and environment of a monument. Under all atmospheric conditions the first deposit is a single layer of brown patina consisting of cuprous oxide Cu_2O (cuprite). When the film reaches the thickness of 8-10 um, the second superficial layer begins to form on its surface. This layer consists of basic cupric salts (the stage of "black patina"). At this stage the cuprous oxide is not replaced by the cupric layer but remains and even thickens a little. The crystal lattice of cuprous oxide (a body-centered cube) is similar to that of copper and its alloys (a face-centered cube). The crystalline affinity of the film structure with its metallic foundation guarantees their structural bondage and the most firm linkage. Thus the presence of an internal film of cuprous oxide in a double layer patina is of prime importance.

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Composition of the superficial layer of patina depends on the presence in the air of different chemically-active impurities gases or fumes (particularly sulfuric gases and chlorides). The superficial layer that appears in industrial atmospheres consists of basic sulfates of copper: brochantite $CuSO_4 . 3Cu(OH)_2$ or antlerite $CuSO_4 . 2Cu(OH)_2$; being formed in an industrial-maritime atmosphere it consists of the above-mentioned sulfates and basic chlorides botallacite, atacamite and paratacamite that have the same composition $CuCl_2 . 3Cu(OH)_2$ but crystallize in different crystal systems (syngonias). Those that were formed in rural environment consist of basic carbonates malachite $CuCO_3Cu(OH)_2$ or azurite $2CuCO_3Cu(OH)_2$. In some cases the superficial layer of patina is formed with a complex mixture of the minerals listed. In addition, in the early stages of its formation it contains traces of neutral (normal) sulfates and chlorides of copper such as $CuCl_2 . 2H_2O$, $CuSO_4 . 5H_2O$ and so on.

Double layer patinas of different compositions have the common name "green patina", though they can have different hues not only of green but also of blue, turquoise, olive and black. The variety of coloration is caused by variations in composition of the superficial layer as well as by both the peculiarities of patina structure (number, sequence, thickness of layers) and optical features (transparency, reflectivity) of minerals. This alone is the reason for the initial black coloration at the early stage of forming a superficial green layer upon the original brown patina.

Substances of which the patina consists have compositions identical to that of the corresponding natural copper minerals and a similar microgranular structure with a grain size equal to 0.1-1 um.

Total thickness of the green patina is 40-80 um, that of the inner layer of cuprous oxide is 10-15 um. Owing to the fact that thickness and granularity have dimensions of different orders, porosity of the patina has a closed nature and therefore it is practically air- and water-proof.

At all stages of its formation this patina has high mechanical qualities.

The Vickers microhardness of the brown patina is on average 190, of black - 91, green - 109 (botallacite), 107 (brochantite), 106 (malachite) kg/sq mm, compared with Vickers hardness of red copper 67-79, tin bronze (40-12,5% Sn; 0,2-0,7% Pb; 0,10-0,50% Zn) 66-91 kg/sq mm. In effect, all kinds of patina are harder than the substance of the monument itself.

Absolute wear resistance for rubbing with fine glass-paper K3-M-28 under a load equal to 1 kg/sq cm is: for brown patina 23-90 (average 49), black 23-48 (average 34), green 90-400 (average 212) cycles. Specific wear resistance, that is, resistance of a unit of film thickness, is accordingly 4,0-6,0 (average 5.1); 2,1-3,0 (average 2,7); 2,4-7,3 (average 4,2) cycles.

When scratched with a sharp steel needle the brown patina acquires grooves with undamaged edges (without cracks, splits or losses). Under these conditions black patina (and in a less degree the green one) has minute splits of the superficial layer where crossed by the scratched groove. These splits are visible under magnification by 25 times. It leads us to think that patina is not fragile and has sufficient plasticity. Quantitatively, the plasticity of a film is characterized as follows: samples being bent around a rod with diameter equal to 3,5 mm begin cracking: those of brown patina at 45-120° (average 100°), of black at 20-35° (average 30°), of green at 20-35° (average 27,5°). With further bending films become loose and peel off from metal. Brown patina begins to peel off when bent at 120-180° (average 158°) but 75% of samples do not peel at all, black peels at 75-90° (average 77°), green at 75-170° (average 126°). Meanwhile, the internal layer of cuprous oxide as a rule does not peel.

The high abrasive- and scratch-resistance and bending strength proves plasticity of the films, their firm cohesion with metal and high resistance to abrasive wear. In conjunction with sufficient thickness and firmness it makes natural patina able

to protect the monument material (body) from mechanical damage. It must be noted that the "black" transition stage is characterized with some deterioration of patina quality but when a green layer is formed its strength increases anew.

Natural patina has high chemical, moisture and heat stability.

Spot tests with a 5% solution of acetic acid (10 min) and with ammonia hydroxide (20 min) result in partial dissolving or strong discoloration (alteration of colour) of brown and black patinas, while the green one remains unchanged or only a little faded. In 3% solution of NaCl (immersion) the appearance of green patina remains unchanged (under the microscope with magnification of 25 times) for 72 hours. The first alteration of brown patina appears in 4 hours, of black in an hour. During the following 72 hours both films change their coloration into blue without physical determination. All natural films withstand 100% relative humidity and 45° C during 15 days without alterations or physical deterioration. Sharp change of temperature from -14°C (1 hour) to + 55°C (immersion into hot water 1 hour) was withstood without visible alteration by the green patina during 35, brown 22, and black 20 cycles. After the indicated number of cycles black and brown films change their hue into green.

The data given on resistance and strength of natural patina toward aggressive agents is not the full story since further examinations were not carried out.

Estimating strength of a film according to the time during which it withstands tests without visible alterations and character of deterioration by the end of examination and using an arbitrary scale of 5 (5 for absolutely stable 1 for absolutely unstable) one can obtain an average value of strength (stability) of each film to the whole complex of aggressive influences.

Table 1

Stability of natural patinas
to aggressive influences

	Stability to influences					
Film name	CH_3COOH	NH_4OH	NaCl	t=45°C, RH=100%	At from -14 to 55°C	Average
Green patina	4-5	5	5	5	5	4,83
Turquoise patina	4-5	5	5	5	5	4,83
Black patina	3	4-5	3	5	4	4,00
Brown patina	3	3-4	3-4	5	4	3,71
Inner layer	4	3	4-5	5	3	4,00

These data prove that stability in aggressive environment increases with the process of conversion of the single-layer oxide film into double-layer green patina. This phenomenon is well explicable, bearing in mind the difference of structures and chemical properties of oxides and basic copper salts. Oxides including cuprous ones are quite stable only in a natural environment. If certain anions are present they become able to cgange chemically. For instance in presence of SO_4^{2-}, CO_3^{2-}, Cl^-, cuprous oxide converts into cupric sulfates, carbonates and chlorides. But the fact that the absolute concentration of the anions listed is very low in the atmosphere while the concentration of oxygen and water is very high results in a very slow rate for reactions which proceed only on the surface of a patina and its products are not neutral but basic salts. The nature of this process is conversion of brown oxide patina into double layer green deposits.

High stability of green patina depends on its density, thickness and so on, as well as on the character and properties of its minerals. All of them are insoluble and chemically stable, being end-products of copper conversion in a natural oxidizing environment, each of them being most stable in the surroundings in which it was formed. It is just this face that determines the absolute atmospheric stability of green patina and makes it able to give reliable protection of monuments from corrosion in any atmospheric condition during an indefinitely long time.

Examples of long-term preservation of copper roofs have a particular importance for evaluation of the quality of green patina as a protective film. In many countries there are roofs with green patina whose age reaches 300-350 years and which notwithstanding have no signs of tubercular corrosion of metal. In Hildesheim (West Germany) the roof of the Cethedral has existed more than 700 years. In the twenties of this century English scientists have established that during a hundred years of the existence of the Bodleian Library roof in Oxford the thickness of copper leaves with which it was covered remained practically unchanged. The fact that in maritime and industrial cities with very aggressive atmospheres there are old roofs of small and unchanged thickness and without any local deterioration is particularly conclusive proof of the high atmospheric stability and excellent protective properties of green patina.

Bearing this in mind, formation of brown and then green patina on out-of-doors monuments is very desirable not only on the ground of aesthetics but also in accordance with out ideas about corrosion and protection of metals. It is in principle possible to install certain monuments with a clean metal surface, which gradually will be covered with a natural patina. But to form a visible oxide film having the customary decorative appearance it takes from six months to a year, to form the green patina it takes from ten to twenty years, and in very pure and dry air, formation of a green patina may take from 100 to 200 years and more.

Taking this into account, most nex-made and restored monuments are covered with an artificial patina. At present many dozens of methods for artificial patination of copper and copper alloys are known. By means of these methods one can obtain a great variety of coatings from the thinnest oxide films to green patina similar to natural ones. All these films are essentially different both in their decorative appearances and in their physical and chemical properties (composition, structure, thickness, continuity, porosity, firmness of cohesion with ground, and mechanical strength, as well as resistance to aggressive influences). But the majority of written (literary) sources in the different languages of the world give only receipts and to some degree practical procedures for forming one or another patina and then point out its color. At best it indicates whether it is strong or not. Therefore, when choosing a method for patination one is guided as a rule not by the properties of a film but by a necessary or desirable color of patina, by conveniences of one or another treatment for a given monument, and by other considerations of aesthetic and technological nature.

No objection is made to observance of these requirements. However, patina is not only a decorative but also a protective film whose physico-chemical properties affect the preservation of a monument at one or another stage of its history. Due to their physico-chemical properties a great number of artifical patinas are sufficiently stable only under museum conditions but in an out-of-doors environment, even with an additional protection by organic coatings (wax, varnish and so on), they become rapidly weathered, filmed with interference tints and spots of discoloration, flaked off, substituted with atmospheric corrosion products of copper and so on. In other words they carry out neither their functions decorative nor protective.

In connection with choosing a patination method for one or another monument it is necessary first to be guided by requirements for the protective properties of a patina in accordance with its

conditions of exposure (closed room, heated or not; out-of-doors, dry, pure, maritime, industrial atmosphere and so on). One must require the most strict specification for monuments to be installed out-of-doors in large cities and industrial or maritime areas. Samples of the artificial patina for such monuments must be examined and tested experimentally in laboratories to determine their physico-chemical properties. The above-mentioned indices, obtained by examination of natural patina, may be used as criteria for evaluation of the results of such testing and examination as well as of the fitness of a given film.

The International Council of
Museums
Committee for Conservation

Conseil International des Musées
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Janusz Lehmann, National Museum, Poznan, Poland.

CORROSION OF MONUMENTS AND ANTIQUITIES MADE OF COPPER AND COPPER ALLOY IN OUT-DOOR EXHIBITS

The advanced and, indeed, precarious state of decay of a large number of historically and esthetically significant monuments and antiquities, that have been subjected to long periods of exposure to water, sun and atmospheric pollutants is evident to even the least observant. As a consequence of the general anxiety for the future existence of this irreplaceable cultural heritage, many institutions and persons resolved to make this problem one of their principal concerns.

The Chemical Laboratory of the National Museum in Poznan and the Institute of Magnetochemistry of A. Mickiewicz University proceeded to an investigation of the corrosion of copper and copper alloys in out-of-doors exhibits. This study was promoted by the Centre of Documentation of Monuments of the Ministry of Culture and Art.

The experiments comprised microscopic, metallographic, spectrochemical, chemical, x-ray and diffractometric analyses. The specimens analyzed were chosen from among copper, bronze and brass relics in four localities in Poland, namely Poznan, Gdansk, Krakow and Lancut. The relics were from thirty to over four hundred years old. Three were of copper, one of brass and two of bronze.

The experimental results were compared with data in the literature. Information concerning results of metallographic, physical and chemical, conservation and technical investigations was taken into account.

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The work reported here has enriched our knowledge concerning the formation of corrosion sediments/patina/ with growing air pollution. Up to now, no unequivocal information about the quantitative proportions of the corrosion products arising on the surfaces of copper and copper alloys undergoing atmospheric corrosion were available. Opinions about the types of chemical compounds occuring in the corrosion products as well as the topography of their occurence differed considerably.

I. Chronological survey of information and opinions relating to corrosion of copper and copper alloy antiquities.

Information and opinions concerning the corrosion of antiquities consisting of copper and its alloys in out-door exhibits can be found in the literature from very ancient times. Among the opinions dating back to the antiquity, those of Plinius and Vitruvius were taken into account and cited.

Scientific investigation of the corrosion products of copper and its alloys in monuments began in the third decade of the XIXth century. Initially it dealt with external aspects of the problem only. Corrosion products on the surface of copper and copper alloy antiquities were identified with the green sediments of the corrosion products occuring on copper utensiles in use at that time. Both the former and the latter were known as verdigris and referred to by the term aerugo, mentioned by Plinius and Vitruvius

The contemporary identification of aerugo based on Viturvius's description concerning its production from metallic copper and vinegar raises no doubts. Investigations carried out in the latter half of the XIXth century showed the identification of corrosion products of copper and its alloys in out-door exhibits, termed "patina", with verdigris, to be incorrect. On the base of chemical and mineralogical analyses, the corrosion products i.e. patina were identified with basic cupric carbonate and referred to the minerals: malachite and azurite. The mineralogical identification of the corrosion products with the minerals malachite, azurite and, later with cuprite, tenorite, covellite, atacamite, brochantite, antlerite, etc. was based on the similarity of outer

features as well as on the content of characteristic elements or groups of elements.

The performing of accurate determinations exceeded the possibilities then available. To identify a mineral, it is necessary to obtain the exact stoechiometric proportions of its components, or to analyse a well grown crystal by optical methods. The corrosion products of copper and copper alloy antiquities always present mixtures of chemical compounds and therefore it is not possible to obtain a precise stoechiometric result. The latter could be obtained only accidentally. It is also impossible to find in the corrosion products such well grown crystals as could be used in a microscopic crystallographic identification.

At the end of the XIXth and the beginning of the XXth centuries publications appeared concerning the conservation of antiquities of copper and its alloy in museums. These publications deal with the reasons, mechanism and results of corrosion. They refer, first of all, to museum and archeological objects, and contain explanations of the corrosion mechanism, stimulated by the presence of halides, sulphides and sulphates.

In the 1930's, comparative investigations of the corrosion of copper and the majority of its alloys were carried out. Among them only brasses exhibited differences in the corrosion process. These alloys undergo dezincification. The majority of the investigated samples, and specifically those being the material of antiquities, behaved very similarly in the course of the corrosion. Consequently, from that time, corrosion of copper and its alloys is dealt with jointly. In the present investigation, no reasons were found for a separate treatment of copper antiquities and ones consisting of copper alloys. Towards the end of the XIX th century, fears began to be expressed because of the blackening of copper and copper alloy monuments in towns. Authors at the time attributed this to stone-coal, which was then beginning to be burnt in towns in considerable amounts. Gaseous and solid atmospheric pollutions arising from coal caused disadvantageous changes in colour on the surfaces of copper and bronze monuments.

Damage from air pollution by fumes is now so evident that efforts are being made to stop the progress of pollution of the medium. Among these problems, the protection of monuments from external pollution by substances causing their rapid destruction has to be given due attention. Air pollution contains solid components, such as soot and dusts, liquid components such as particles of oils, pitch and fog saturated by gases soluble in water, and gaseous components such as sulphur dioxide, carbon monoxide and dioxide, hydrogen sulphide, and nitrogen oxides. These pollutions are present everywhere. Their quantity depends on place and time. The greatest fear is now inspired by sulphuric gases. The content of sulphur dioxide in pure air does not normally exceed 20 micrograms per 1 cubic meter. This amount is usually reckoned as unharmful. Living organisms are able to adapt themselves to contents of sulphur dioxide in air many times larger. Relics consisting of textiles, paper, leather or parchment as well as paintings on a limy and hydrous binder are unable to adapt and are the most sensitive to sulphur dioxide.

The concentration of sulphur dioxide which begins to be harmful for the above mentioned types of relics has been estimated variously. The values given by authors lie between 100 and 200 micrograms of sulphur dioxide per 1 cubic meter of air.

In Poland, in regions of greatest smokiness, the sulphuric acid concentration on foggy and windless winter days attains several thousand micrograms per 1 cubic meter of air. According to the opinion of certain authors, this content doubles every 10 years, whereas according to others every 20 years. The problem of pollution by other by-products of the progress of civilization stands similarly.

The darkening of polished and unprotected surfaces observed when the content of hydrogen sulphide in air attains 500 micrograms per $1 m^3$ can inform us about the order of magnitude of the pollution influencing copper and its alloys. One can assume that the threshold of harmfulness i.e. the smallest content of sulphuric gases in air which causes acceleration of the corrosion of copper and its alloys amounts to several hundred (from 300 to 500) micrograms per cubic meter of air, in accordance with the opinion of the majority of authors studying the harmfulness of gaseous pollution.

Opinions regarding the corrosion of copper and its alloys in pure air agree. In the initial stage, cuprous oxide analogous to the mineral cuprite is produced. With respect to corrosion of copper and its alloys in the air polluted by halides, sulphur dioxide, hydrogen sulphide, nitrogen oxides and other chemical compounds stimulating corrosion of copper, opinions still differ, probably for a lack of available experimental data. The corrosion products arising in air polluted by sulphuric compounds consist mainly of sulphides and basic cupric sulphates. In the course of time, cupric sulphide undergoes oxidation to sulphate. Basic cupric sulphates occur in these corrosion products in the form of antlerite according to some authors, or in the form of brochantite, according to others. Some maintain that the chief component occuring in out-door exhibits is still basic cupric carbonate, analogous to malachite or azurite. According to this opinion, even when basic cupric sulphate or basic cupric halide appears, in the initial stages of corrosion, a suitable cycle of transformations under the influence of moisture, carbon dioxide and oxygen finally leads to cupric carbonate.

Yet others maintain that basic cupric carbonate under the influence of hydrogen sulphide or sulphur dioxide finally transforms to a basic cupric sulphate analogous to bronchantite or antlerite. Similarly, under the influence of halide pollutions, basic cupric carbonate transforms to a basic cupric halide analogous to atacamite or paratacamite. Basic cupric halide affected by sulphur dioxide or hydrogen sulphide undergoes a transformation to basic cupric sulphate, whereas basic cupric sulphate does not transform to basic cupric halide under the influence of halide pollutions. The latter opinions have as yet been neither confirmed finally nor proved to be false. It cannot be denied, that the corrosion products, more particularly their surface layers, contain sulphates, carbonates, halides, sulphides and oxides concomitantly. Cupric compounds exhibit auto-reduction; thus, secondarily precipitated metallic copper can occur, as confirmed experimentally.

Products of the corrosion of copper and its alloys which are resistant in some conditions can undergo further transformation when put in other conditions. These transformations are apparent

as changes in tint and structure in the sense of mechanical properties. It would seem that the quantitative proportions of the various components in the surface layer agree with the proportions of the chemically active atmospheric components. The composition of corrosion products can vary widely. Up to now, the following chemical compounds have been identified in the products of corrosion of copper and its alloys:

a/ cuprite,
b/ malachite,
c/ tenorite or melaconite,
d/ azurite,
e/ chalcocite,
f/ digenite,
g/ covellite,
h/ chalkopyrite,
i/ stannite,
j/ nantokite,
k/ caledonite,
l/ atacamite,
m/ paratacamite,
n/ brochantite,
o/ antlerite,
p/ bornite,
r/ enargite,
s/ botallackite,
t/ chrysocolla,
u/ gerhardite
w/ chalconatronite,
z/ libethenite.

The identification of these various cupric compounds in the corrosion products became possible owing to the introduction of roentgenography and diffractometry in the examination of corrosion products. The earliest identifications of corrosion products of copper and its alloys in relics were performed by x-ray diffractometry between 1930 and 1933. Identification of various compounds contained in the corrosion products of copper and its alloys is being pursued more intensely since 1950. They concern however, mainly museum objects and archeological discoveries in indoors exhibits. Hitherto no x-ray examinations of products of copper and copper alloy corrosion in out-door exhibits and subaquaceous archeological excavations have been performed.

The last twenty years have witnessed considerable progress in analytic-structural studies, due to the introduction of more highly perfected equipment, such as diffractometers, electron microscopes, electron probes and neutronographs into experimental practice.

The electron microscope permits magnifications more than ten times exceeding the possibilities of the optical microscope. Difficulties of electronic microscope technique are connected with the preparation of specimens. Since metallographic specimens are not penetrable by electrons and observation in reflected electron rays is not possible, in metallographical analysis the examination of replicas is resorted to. Such impressions, made by applying an artificial material, most frequently methacrylate, to the surface of the examined metal, fix in the negative the structural details of the surface or section of interest to us. Separated from the surface, the impressions are usually coated with a thin layer of metal by the shadow method in order to improve contrast.

In the electron microprobe, the examined material is illuminated with a strongly collimated electron beam, the diameter of which does not usually exceed 1 micron. The x-rays excited by the incident beam are examined with an x-ray spectroscope. Spectrum recording is performed by a counter system and an electronic counting circuit. The recording is obtained in the form of a strip-chart in a self-recording equipment. The optical microscope built into equipment permits observation of the analyzed surface. Such equipment permits detailed examination of extremely small amounts of material.

Neutronography is a development of the x-ray diffraction method. Instead of x-rays, the analyzed material is illuminated with a neutron beam. The neutrons undergo diffraction similarly as the x-rays. The difference resides in the fact that the x-rays undergo diffraction on the electron shells of atoms, whereas the neutrons penetrate through the electron shell and undergo diffraction on the atomic nuclei. We mention the methods of electron spectroscopy, the electronic microprobe and neutronography in the present report since the first investigations of antiquities and works of art by these methods have already been published. Moreover, it is hoped to obtain experimental data which will permit solution of numerous problems concerning the corrosion of copper and copper alloys in out-door exhibits by means of the above mentioned equipment.

II. Identification of corrosion products.

1. Experimental technique.

The experiments comprised microscopic-metallographic observations, spectrographical, chemical and photocolorimetric analyses and x-ray and diffractometric examinations. The specimens analysed were chosen among copper, bronze and brass monuments in four localities in Poland, namely Poznan, Gdansk, Krakow and Lancut. The monuments were from thirty to over four hundred years old.

a/ Sampling. Six different types of corrosion products, representative of the broad range of properties encountered in practice were employed in these investigations. They were as follows:

Marking of Samples

Table No. 1

Sample No.	Monument	Climate	Metal	Age	Colour of surface	Condition of examined material.
1.	Statue of Hygea at Poznan	town	bronze	80 y.	green-black-rusty	metallic-non transformed
1a.	"	"	"	"	"	corroded-transformed
2.	Tower roof of Jesuit Church at Poznan	"	copper	200 y.	green black	metallic-non transformed
2a.	"	"	"	"	"	corroded-transformed
3.	Statue of St. George Gdansk	maritime town	copper	400 y.	green black	metallic-non transformed
3a.	"	"	"	"	"	corroded transformed

Table No. 1 cont.

4.	Gutterpipe Landcut - Castle	small town, rural	copper	200 y.	green	metallic
4a.	"	"	"	"	"	corroded
5.	Cannon Cracow - Castle	town industrial	bronze	350 y.	green-bluish-brown	metallic
5a.	"	"	"	"	"	corroded
6.	Statue of a young man Poznan	town	brass	30 y.	black-brown	metallic
6a.	"	"	"	"	"	corroded

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b/ Microscopic examination. In the microscope examinations, a Zeiss Nf optical microscope was used, with special condensers for analyzing in reflected polarized light. The optical equipment of the microscope, of high precision, consisted of apochromatic and planachromatic objectives and compensation eyepieces. In the experiments, magnifications of 100 and 300 times were used.

The samples in the form of sections through the corrosion products and metal were immersed in subsequently hardened epoxy resin Epidian 5. The sections were ground off and polished wet with carborundum powder. In order to obtain contrasted pictures of crystals and intercrystalline spaces as well as of the metallic and corroded phases, colour filters were used for the illuminator.

Microscopic examinations in all six cases showed the corrosion products to split distinctly into two parts. On the very surface, a thin layer is distinct (thickness from 0,005 to 0,05 mm) of amorphous green, green-blue and black sediments inter-grown with adhering grains of dust, soot, etc.

In sample No. 6, brown and black sediments were predominant in the latter layer.

Beneath the thin surface layer, there is an inner layer of corrosion products several or 10 - 20 times thicker and considerably different from the outer layer. The predominant colour here is red and red brown. In this layer, the contours of the initial metallic structure consisting of grained crystals and intercrystalline spaces are distinguishable. Green and bluegreen tints occur sporadically in the form of damp patches and shadows, mostly in the neighbourhood of the boundary with the thin surface layer. The boundary separating the thin surface layer from the inner layer of corrosion products is almost always sharp, whereas the boundary between the inner surface and the metal is mostly diffuse. Deep intrusions of intercrystalline corrosion into the bulk of the metal are visible, particularly in the specimens taken from objects several hundred years old.

c/ Spectral emission analysis. By spectral emission analysis, samples of the metal and corrosion products were examined in order to determine the majority of the elements contained in the analyzed material. The contents of main components of the metal and admixtures and pollutions were determined in significant and trace quantities. Two types of the determinations were carried out, namely qualitative and semiquantitative.

The investigations were performed with an ISP 22 spectrograph for review examinations at three-lens illumination, a 0,01 mm slit, and excitation in an AC electric arc of current intensity 15 A between coal electrodes. The spectrographic plates were of hard grade, size 9 x 24 cm. The lines were read on a Zeiss/Jena/SP 2 spectroprojector.

In the reports of semiquantitative determinations, a conventional table was used in which the number 5 signified a content larger than 10%, the number 3 - a content in the range from 1 to 10%, the number 1 - a content below 1%. Trace contents were marked by the sign +.

The results of qualitative determinations appear in Table No 2., and those of the semiquantitative in Table No 3. During the qualitative determinations we have chosen the most suitable lines.

Spectrographic qualitative determinations.

Table No. 2.

ne	5105	4524	4057	5209	3961	4722	4425	3745	5167	4035	4314	3905	4680
ment	Cu	Sn	Pb	Ag	Al	Bi	Ca	Fe	Mg	Mn	Sc	Si	Zn
mple o.													
1.	+	+	+	+	-	-	-	-	-	-	-	-	+
1a	+	+	+	+	+	-	+	+	-	-	-	+	+
2.	+	-	-	+	-	-	-	-	-	-	-	-	-
2a	+	-	-	+	+	-	-	+	+	-	-	+	+
3.	+	-	-	+	-	-	-	-	-	-	-	+	-
3a	+	-	-	+	-	-	+	-	-	-	-	+	-
4.	+	-	-	-	-	-	-	-	-	+	+	-	-
4a	+	-	-	-	-	-	+	-	-	+	+	+	-
5.	+	+	+	+	-	-	-	+	-	-	-	+	+
5a	+	+	+	+	+	+	+	+	+	-	-	+	+
6.	+	+	+	-	+	+	-	-	+	+	-	+	+
6a	+	+	+	+	+	-	-	+	+	-	-	+	+

Spectrographic semiquantitative determinations.

Table No. 3.

lement ample	Cu	Sn	Pb	Ag	Al	Bi	Ca	Fe	Mg	Mn	Si	Zn
1.	5	3	3	+	-	-	-	-	-	-	-	+
1a	5	3	1	+	+	-	+	+	-	-	+	+
2.	5	-	-	+	-	-	-	-	-	-	-	-
2a	5	-	-	+	+	-	-	+	+	-	+	+
3.	5	-	-	+	-	-	-	-	-	-	+	-
3a	5	-	-	+	-	-	+	-	-	-	+	-
4.	5	-	-	-	-	-	-	+	-	-	-	-
4a	5	-	-	-	-	-	+	+	-	-	+	-
5.	5	3	3	+	-	-	-	+	-	-	+	3
5a	5	3	3	+	-	-	+	+	+	-	+	1
6.	5	3	3	-	+	+	-	-	+	+	+	3
6a	5	3	3	-	-	+	-	+	+	-	+	3

5 = above 10%

3 = from 1 to 10%

1 = below 1%

+ = traces.

The occurrence of various trace elements, beside the main alloy components such as copper, tin, lead and zinc as well as normally occurring additions such as silicon, aluminium, phosphorus, was revealed by the spectrographic analysis. For example, the occurrence of silver is characteristic. The latter was exhibited by all the specimens with the exceptions of the Lancut specimen and specimen No. 6. The specimen No. 6 represents contemporary brass-bronze, containing electrolytically refined copper, whereas in the Lancut specimen the copper comes from other place than in the remaining analyzed monuments.

The information obtained by way of spectrographic analysis can be used in studies concerning the places of origin as well as in a technological study of the analyzed objects, particularly with regard to the occurrence of trace elements. In the interpretation of the results, the possibility that some elements could be deposited from atmospheric pollution and that elements sedimenting in the intercrystalline spaces of the metal could diffuse into the corrosion products is taken into consideration.

The occurrence of trace elements does not influence the corrosion process. It can however explain the appearance in the corrosion products of such compounds as: $CuAsS_4$ - enargite, $CuOHPO_4$ - libethenite and $CuFeSnS_4$ - stannite. The chief aim, however, of the present spectrographic analysis was to determine the general composition of the metal and corrosion products in the analyzed specimens which facilitated and rendered more accurate the course of quantitative analysis.

d/ Chemical analysis. The quantitative determinations were performed by the methods of weight, volumetric, gasometric and photocolorimetric analysis. Weight analysis was used in determining the contents of moisture, heating losses, and parts soluble in water, sulphuric acid, nitric acid, aqua regia as well as insoluble. With regard to the considerable differences in composition of the surface and inner layers of the corrosion products, sample determinations were performed for the surface layer.

The gasometric method was applied for determining the content of CO_2 in the corrosion products. To measure the quantity of gas set free, a burette with 0,05 ml scale was used. Available were charges ranging from several hundred milligrams to over 1 gram. The smallest determinable quantity of carbonic dioxide amounted to nearly 0,1 mg, i.e. was below 0,1%. The method used here permitted to attain accuracy of this order.

By volumetric methods, the main metallic components and, moreover, sulphates and halides were determined. The sensitivity and accuracy of the volumetric method in determinations of sulphides, halides and sulphates was similar to that used in determining carbon dioxide.

Because of the relatively large amounts (about 0,1 g) necessary for performing volumetric and gasometric determination, these methods were not adequate for determining the contents of traces in the analyzed metals and corrosion products.

The results of quantitative determinations appear in Tables No. 4 and No. 5.

In the discussion of the results no attempt was made to perform stoichiometric recalculations. Such calculations would be apt to lead to casual results because of the complicated composition of the metals and corrosion products, representing mixtures. Results approximating stoechiometric ones obtained in the analysis of alloys only. The deficiences attaining tenths fractions of 1% in the content of an element can be explained by the presence of oxides, which was confirmed by microscopic examinations. In the analyzed copper and copper alloy specimens, the occurrence of the oxides was due to the technology of metallurgic production as well as to intercrystalline corrosion.

Weight analysis.

Table No. 4.

Sample No.	contents %					
	drying losses	heating losses	parts soluble in water	in H_2SO_4	in HNO_3	Ins
1.	-	-	-	95,1	89,1	0,2
1a	0,02	3,1	0,05	93,2	85,3	6,8
2.	-	-	-	98,5	96,7	1,5
2a	0,03	2,9	0,07	91,2	92,4	7,6
3.	-	-	-	98,7	95,7	1,3
3a	0,05	3,7	0,1	95,5	93,7	4,5
4.	-	-	-	97,9	96,2	2,1
4a	-	2,9	-	95,1	95,3	4,7
5.	-	-	-	94,7	86,1	0,2
5a	0,05	3,5	0,1	93,2	88,2	6,8
6.		-	-	92,6	93,4	0,1
6a	0,02	2,8	0,05	92,8	95,1	4,8

Volumetric and gasometric analysis.

Table No. 5

Sample No.	contents %							
	Ag	Cu	Pb	Sn	Cl	CO_2	S	SO_3
1.	0,01	87,2	1,7	10,1	-	-	-	-
1a	0,03	45,2	2,8	11,3	tr.	1,2	0,2	0,6
2.	tr.	98,8	-	-	-	-	-	-
2a	tr.	52,3	-	-	-	2,4	0,3	0,7
3.	tr.	98,3	-	-	-	-	-	-
3a	tr.	51,2	-	-	0,1	2,3	0,4	1,1
4.	-	98,1	-	-	-	-	-	-
4a	-	50,3	-	-	tr.	2,6	0,1	0,3
5.	tr.	80,7	3,5	13,1	-	-	-	-
5a	tr	43,1	4,1	17,2	-	3,2	0,1	1,3
6.	-	88,1	1,0	8,7	-	-	-	-
6a	-	57,3	1,2	12,1	tr.	0,3	0,4	0,6

e/ Analysis of trace elements. The trace elements as well as the main components of the alloys were moreover determined photocolorimetrically in order to verify the weight, volumetric and gasometric results as well as to confirm the results of spectral analysis. The sensitivity of photocolorimetric methods exceeds at least several hundred times that of the volumetric methods. The smallest amounts accessible to determination are of the order of 10^{-4} mg. As unit of the content, in photocolorimetric determinations, 1 microgram per mililitre is assumed i.e. 1/1000th of a milligram per 1 cubic centimetre of the tinted solution. This high sensitivity restricts accuracy of the method. This limitation is due to the method of photocolorimetric measurement and to the methods of separation of the elements analyzed. The methods used in separation trace elements consisted in conversion into a tinted complex and extraction of the latter into an organic solvent not mixing with water.

The extraction method was supplemented by a masking of perturbating elements by their conversion into a complex more durable than the tinted complex previous to extraction of the latter (the one containing the element to be determined).

In order to avoid error caused by casual composition of the analyzed sample, taken from a casual place and in a too small amount, the samples for extraction were taken from the solution of a larger sample. Thus, a possibly uniform diffusion of the components of each sample was obtained.

In the undissolved specimen, particularly of corrosion products, the various components were not uniformly distributed, as shown clearly by microscopic examination. Therefore, in the spectrographic determinations, qualitative results were admitted. The results of semi-quantitative determinations were also considered as purely indicatory.

Neither can one overrate the accuracy of the photocolorimetric determinations. Even when taking the specimen for determination from a possibly large dissolved sample and observing strictly identical conditions in determining the elements of the sample and model solutions (standard solutions), a possibility of error

Photocolorimetric determinations

Elements in significant quantities.

Table No. 6.

Sample No.	Contents %			
	Cu	Sn	Pb	Zn
1.	87,0	1,5	1,0	0,4
1 a	46,0	11,0	3,0	0,2
2.	99,0	-	-	-
2a	52,0	-	-	-
3.	98,0	-	-	-
3a	51,0	-	-	-
4.	98,0	-	-	-
4a	50,0	-	-	-
5.	81,0	13,0	3,0	2,0
5a	43,0	17,0	4,0	1,0
6.	88,0	9,0	1,0	1,3
6a	57,0	12,0	1,0	0,5

Trace elements.

Table No. 7.

ample No.	contents %									
	Ag	Al	As	Bi	Fe	Ni	P	Pb	Si	Zn
1.	0,005	-	-	-	-	-	-	/1,0/	0,01	/0,4
1a	0,009	0,02	0,002	-	0,7	-	0,009	/3,0/	1,3	/0,2
2.	0,001	-	0,01	-	-	0,001	-	-	-	-
2a	0,001	0,04	0,007	-	0,09	-	-	-	2,2	-
3.	0,03	-	-	-	-	-	-	-	0,2	-
3a	0,25	-	0,08	-	-	-	-	-	1,3	-
4.	0,002	-	0,02	-	-	-	-	-	0,04	-
4a	0,01	-	0,01	-	-	-	0,003	-	0,5	-
5.	0,01	-	0,003	-	0,004	-	0,01	/3,0/	0,01	/2,
5a	0,02	0,02	0,002	0,02	0,03	0,005	0,07	/4,0/	2,2	/1,
6.	-	0,007	-	0,004	0,09	-	-	/1,0/	0,05	/1,
6a	0,003	0,009	-	-	0,15	-	-	/1,0/	0,7	/0,

exceeding 10% always exists if the content is very low. In order to reduce the influence of elements present in the specimens in amounts many times exceeding the content of an analyzed element on the results of photocolorimetric analysis, the accompanying elements were added to the standard solutions in amounts of the same order as in the samples.

Photocolorimetric determinations were performed with an Hungarian Uvifot photocolorimeter equipped with sets of glass and quartz cuvettes, a source of ultra-violet light (low-pressure quartz-lamp), two photoelectric cells, and optical compensator and oscilloscopic zero indicator. Monochromatic light was obtained using filters in following lengths of light waves: max. 254, 313, 366, 405, 436, 480, 510, 546, 578, 625 and 675 milimicrons.

f/ x - ray diffraction analysis. The x-ray diffraction determinations were performed with a Siemens x-ray Powder Camera. The cylindrical camera had a diameter 57,3 mm and a height of about 160 mm. The film is held on its inner surface, and a cap is fitted over the top to keep out light during exposure.

The powder photographs of samples taken with the powder camera have been read by Zeiss Microphotometer.

Mostly has been used the copper radiation of microfocus x - ray tube, working at 30 - 40 kV, 3 - 4 mA. The exposures were 30 - 60 minutes.

The results of x-ray diffraction were as follow.

Sample 1

O	d
50° 42'	2.0890
58° 54'	1.8192
87° 36'	1,2923
108° 24'	1,1023

Sample 1a

O	d
17°48'	5,73
21°6'	4,88
25°0'	4,13
28°30'	3,63
31°12'	3,326
34°30'	3,016
37°6'	2,811
38°18'	2,727
43°12'	2,430
50°18'	2,105
59°30'	1,802
65°18'	1,659
73°0'	1,504
74°24'	1,479
78°12'	1,418
88°12'	1,285
92°54'	1,2402
108°24'	1,1000
113°48'	1,0676
131°42'	0,98024
138°48'	0,95556

Sample 2

O	d
50°24'	2,101
58°54'	1,819
72°18'	1,516
87°36'	1,292
94°24'	1,2190
108°24'	1,1028
115°42'	1,0564

Sample 2a

O	d
33°54'	3,07
42°24'	2,473
44°18'	2,372
49°30'	2,136
58°24'	1,833
61°36'	1,747
72°12'	1,518
85°6'	1,323
92°18'	1,240
107°18'	1,110

Sample 3a

Θ	d
23°12'	4,45
24°36'	4,20
31°30'	3,295
34°42'	2,999
41°42'	2,513
43°0'	2,441
46°0'	2,289
49°54'	2,120
51°6'	2,074
53°54'	1,974
57°12'	1,868
59°30'	1,802
70°42'	1,546
72°42'	1,516
81°36'	1,369
88°0'	1,288
88°48'	1,278
90°42'	1,2572
93°18'	1,2300
96°24'	1,1938
98°36'	1,1797
110°30'	1,0885
113°48'	1,0676
118°6'	1,0429

Sample 4a

Θ	d
16°36'	6,20
17°30'	5,88
19°54'	5,18
20°42'	4,98
21°48'	4,73
24°42'	4,18
27°12'	3,80
28°12'	3,67
31°12'	3,326
34°30'	3,016
37°0'	2,819
37°48'	2,761
41°54'	2,502
42°48'	2,451
44°48'	2,347
46°12'	2,279
48°24'	2,182
49°54'	2,120
51°24'	2,061
53°48'	1,977
54°54'	1,939
56°12'	1,899
58°48'	1,822
59°42'	[illegible]

Sample 5 a

Θ	d
18°48'	5,48
20°0'	5,15
23°30'	4,39
26°12'	3,94
28°0'	3,70
30°0'	3,46
31°6'	3,336
34°30'	3,016
36°18'	2,871
38°18'	2,727
42°54'	2,446
46°54'	2,248
50°0'	2,116
52°30'	2,022
54°0'	1,970
56°18'	1,896
57°30'	1,859
59°12'	1,811
61°30'	1,749
63°24'	1,702
64°30'	1,676
67°54'	1,602
70°30'	1,549
72°54'	1,505

g/ X - Ray Recording Diffractometry.

The x-ray diffractometry was performed with Siemens X-ray Diffractometer which records diffraction patterns automatically. The diffractometer is equipped with scintillation and Geiger-Muller counters, with scanreversing mechanism, powder specimen holder, two Soller slits, semi-proportional counter, goniometer, pulse amplifiers, pulseheight analyser and discriminator, scaler ratemeter, ratio recorder. The most important parts of equipment are microfocus x-ray tube, Weisenberg-Bohn goniometer, Geiger-Muller or scintillation counter, head amplifier and electronic console including recorder.

The results of diffractometric analysis are presented in form of specimen trace pattern.

We have identified in corrosion products of monuments and antiquities in out-door exhibits the following components:

- Cu_2o - Cuprite,
- CuO - tenorite or melaconite,
- $Cu_2CO_3./OH/_2$ - Malachite,
- $Cu_3/CO3/_2/OH/_2$ - Azurite,
- Cu_2S - chalcocite,
- CuS - covellite,
- Cu_2FeSnS_4 - stannite,
- $Cu_2/OH/_3Cl$ - atacamite,
- $Cu_4SO_4/OH/_6$ - brochantite,
- $CuCl$ - nantokite,
- $CuSiO_3.H_2O$ - chrysocolla,
- $Cu_2. OH . PO_4$ - libethenite,
- metallic copper, tin, lead and zinc. In sediments we have found also reduced in autoreduction reaction metallic copper. The diameters of crystals have been variable from 10^{-6} mm to 10^{-2} mm. In young corrosion sediments we have found very small crystals, old corrosion products well grown crystals.

III. Conclusions.

1. The corrosion products on the monuments and antiquities of copper and copper alloys in out of doors exhibits arises under the influence of moisture, oxygen and air pollution.

2. The corrosion products are derived from copper and other components of alloys. They are formed as a thin layer of sediments on the surface and several thicker layers of corrosion products under the primary surface of metal.

3. The composition of the outer layer of sediments depends on the composition of metal and on the nature of air-pollutants. The air pollution influences very little the composition of the inner layer of corrosion products of copper and its alloys in out-door exhibits.

4. Corrosion products on the surface of copper and copper alloy monuments and antiquities in out-door exhibits contain active atmospheric components bounded with atoms of metals and solid atmospheric pollutants such as soot and dust.

5. The presence of copper sulphides, copper sulphates and chlorides proved that products of the corrosion of copper and its alloys which are resistant in pure air undergo further transformations when put in polluted atmosphere.

6. The deeper layers of corrosion products contain mostly cuprous oxide. In this layer of corrosion products, the contours of the initial metallic structure consisting of grained crystals and intercrystalline spaces is distinguishable in many cases.

7. Green and bluegreen tints occur sporadically in the form of damp patches and shadows, mostly in the neighbourhood of the deep intrusions of intercrystalline corrosion into the bulk of the metal. These are visible particularly in the specimens taken from objects several hundred years old.

8. In the corrosion products we have found compositions identical with the following minerals: cuprite, tenorite, chalcocite, covelite, nantokite, malachite, azurite, stannite, atacamite, brochantite, chrysocolla, libethenite.

9. The experiments reported here have enriched our knowledge concerning the influence of air-pollution on the formation of corrosion products and sediments, called "patina" on bronze and bronze alloy monuments and antiquities in out-foor exhibits.

10. The experiments will be continued in order to obtain more experimental data which will improve the possibilities to solve numerous problems concerning the corrosion of copper and copper alloys in out-door exhibits.

Bibliography

1. Reitemeyer J.F., Geschichte des Bergbaues und Huttenwesen bei den alten Volkern. Gottingen 1785.
2. Chevreul. La composition chimique d'une statuette de bronze trouvé par Mariette dans l'Egypte. Comptes Rendus, Paris 1856.
3. Reuss. Einige Produkte der chemischen Umwandlung auf einigen Celtischen Bronzen letztens in Tschehei gefunden. Neues Jahrbuch für Mineralogie, Geognosie u Petrefaktenkunde, Wien 1860.
4. Lenz H.O., Mineralogie der alten Griechen u. Romer., Gotha, 1861.
5. Magnus D., Uber die Einfluss der Bronzezusammensetzung auf die Erzeugung der schonen grunen Patina. Dinglers Polytechn. Journal, 1884.
6. Donath E., Kunstliche Patinierung. Dinglers Polytechnisches Journal, 1884.
7. Kayser R., Uber die Patinierung von Denkmaler. Kunst u. Gewerbe, Munchen 1886.
8. Groger M., Uber Kupferkarbonat. Zeitschrift d. anorganischen Chemie, No. 24, 1900.

9. Rhousopoulos O.A., Die Reinigung u. Restaurierung der archaologischen Altertumsfunden. Museumskunde, vol. 7, 1911.

10. Benner R.C., Effect of smoke on metals. Mellon Institute Bulletin No. 6, 1913.

11. Bode F., Patinierung d. Bronzen in alter u. neuer Zeit. Museumskunde vol. 6, 1910.

12. Fischer O.W., Die Patina der Grossstadt. Wiener Bauindustrie Zeitung. 1914 (n° 24).

13. Vernon W.H.J., Reports to the atmospheric corrosion. Transactions o. Faraday Society, 1923, 1926, 1927, 1929.

14. Weiser H.B. a. Milligan W.O., X-ray studies on the hydrous copper oxides. Journal o. Physical Chemistry. vol. 36, 1932.

15. Gettens R.J., Composition of the patina on a modern bronze statue. Technical Studies i.t. Field of Fine Arts. Smithsonian Institution, vol. 2, 1933.

16. Plenderleith H.J., Some aspects of museum laboratory work. Chemistry a. Industry, 60, 1941.

17. Imhoff C.E., Identification of corrosion products according to crystal structure. vol. 9, 1953.

18. Lehmann J.O., konserwacji zabytkow metalowych. Studia Muzealne, vol. 1, 1953.

19. Gettens R.J. a. Frondel C., Chalconatronite: an alteration product on some ancient Egyptian bronzes. Studies in Conservation, 2, 1955.

20. Plenderleith H.J., The Conservation of antiquities and works of art. Oxford University Press, 1956.

21. Lehmann J., Na marginesie konserwacji zabytkow srebrnych ze zbiorow Muzeum Narodowego w Poznaniu. Muzealnictwo 10, 1961.

22. Organ R.M., A new treatment for bronze disease. Museums Journal, 61, 1961.

23. Lehmann J., Badania i prace nad metodyka konserwacji zabytkow etnograficznych i archeologicznych. Ochrona Zabytkow XV, 1962.

24. Neuhaus A. a. Gebhardt M., Krystalline Korrosionschichten auf Metallen und ihre Beziehung zur Epitaxie. Werkstoffe u. Korrosion, 17, 1967.

25. Zuber K., Neutron activation analysis of Roman copper coins. Atomic Energy Commission. Accession Report, 1966.

26. Gettens R.J., The Freer Chinese Bronzes. vol. II, Smithsonian Institution, vol. 7, 1967.

27. Molinski S., Problemy korozji w zwiazku z uprzemyslowieniem kraju. Chemik, 20, 1967.

28. Smolczyk H.G., Zur Roentgen Feinstrukturbeugung als mineralogisch- analytisches Verfahren. Zeitschrift d. Physicalischen Chemie, 53, 1967.

29. Lehmann J., Patyna na zabytkach metalowych. Monografie Muzeum Narodowego w Poznaniu, vol. II, 1968.

30. Lehmann J., Metody konserwacji zabytkow metalowych, kamiennyc i ceramicznych. Rocznik Muzeum Rolnictwa w Szreniawie, vol. 3, Poznan 1971.

RECHERCHES SUBAQUATIQUES
A HAN-SUR-LESSE.

Depuis juillet 1963 ,-- à la suite de la découverte fortuite, faite au fond de la Lesse par Marc Jasinski, de poteries du Moyen Age ainsi que d'une hache à ailerons et d'un couteau à douille du Bronze final --,des plongées ont lieu dans la Lesse, près de la sortie de la Grotte de Han (à Han-sur-Lesse,province de Namur,Belgique),à la base de la plage qui s'étale devant la Galerie des Petites Fontaines et en aval de celle-ci.

Sur une longueur de 36 mètres et sur une largeur de 4 à 12 mètres fut placé,au fond de la rivière,un quadrillage,composé de carrés de 2 m sur 2 m,en cornières de fer et munies de pieds; ces carrés sont désignés par une lettre et un chiffre,marqués sur des carrés de plastique de o,lo m de côté,de plastique jaune. Certains repérages supplémentaires sont effectués à l'aide de bouées oblongue sur plombs.

A l'intérieur de chaque carré,de l'aval à l'amont,se fait systématiquement la mise à nu de la couche archéologique et l'enlèvement de cette strate par aspiration. Les objets considérables sont enlevés à la main,le reste est recueilli après suçage.

Le schéma général de l'installation comporte un compresseur, le tuyau à air comprimé,le tuyau de suçage et un tamis flottant.

Le compresseur Atlas Copco a une force de 45 HP avec une capacité de 5 M3 par minute;à cause de la répercussion du bruit dans la grotte,l'engin a été placé à 2oo mètres du lieu de travail.

L'air comprimé est amené à l'aide d'un tuyau sans raccords,de 1 1/4 pouce en socarex et possédant une clef à son extrémité inférieure; à hauteur du tamis, il possède une vanne et une bifurcation pour la projection d'air.

Le tuyau de suçion,d'une longueur de lo mètres pour le travail par 7 mètres de fond, et d'une longueur de 5 mètres pour 2 mètres de fond,est soutenu par deux flotteurs d'une capacité de 5 litres pour l'obtention d'une courbe harmonieuse; ce tuyau a un diamètre intérieur de o,15 m et possède un embout inférieur, muni de deux poignées et de forme légèrement tronconique, pour éviter le calage de cailloux Il peut être muni d'une coiffure à croisillon.

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L'embout est manoeuvré par un plongeur fortement plombé et revêtu d'un combinaison double, la température de l'eau pouvant être de 4º et n'atteignant 15º que dans des circonstances exceptionnelles. Dans cette rivière sous voûte et pouvant présenter sur le chantier une profondeur de 10 mètres, la visibilité est très mauvaise et atteint rarement le distance d'un mètre dans les circonstances optima, par temps froid en hiver. Le plongeur dispose pour le dépôt de grands objets directement recueillis, d'un seau percé de trous et lesté de plomb.

Les recherches subaquatiques de Han-sur-Lesse ont livré jusqu'à présent une tres grande quantité d'objets de différentes époques: Néolithique, Bronze final, La Tène initial et final, périodes romaine et mérovingienne, Moyen Age et XVI-XVIIº siècles, époques durant lesquelles la grotte servit d'habitat de refuge, plus rarement de ~~comme~~ sanctuaire.

Les objets recueillis sont transmis à l'atelier du département de la Belgique Ancienne, aux Musées Royaux d'Art et d'Histoire, à Bruxelles, pour y subir un traitement en vue de leur conservation. De nombreux objets de bronze, pour la plupart appartenant au Bronze final (groupe helvéto-rhénan des Champs d'Urnes, phases Ha A 2 à B 3) sont démunis de patine ou présentent une légère patine fluviale dorée; leur état de conservation est parfait et ne nécessite aucune autre intervention qu'un lavage. D'autres présentent une patine terrestre verte à vert foncé; des encroûtements calcareux sont enlevés mécaniquement. Un petit nombre ont subi des atteintes de rouille et la formation d'un fausse patine qui est enlevée dans ses parties atteintes à l'aide de petits disques et cônes de carborundum.

De nombreuses haches à douille renfermaient l'extrémité du manche de bois, conservé par oxydation; une hache possédait encore les trois quarts de son manche de bois de chêne: Ce manche, devenu très mou, a été traîté par une séjour de neuf mois dans des bains de carbowax; le résultat a été très satisfaisant, aucune torsion ou fissuration ne s'étant manifestée.

De nombreux morceaux de cuir, provenant de chaussures médiévales ont été traîtées par imprégnation. de Carbowax ou par bains de Méthanol et d'éther.

Parmi les objets de fer, une grande pointe de lance à ailerons, du Haut Moyen Age, a été traitée par Mr. France-Lanord, au Musée Lorrain de Nancy; le traitement a révélé une partie centrale à damassage.

Une grande partie des tessons de poteries appartient au Bronze final; de nombreuses poteries fines ont conservé leurs incrustations blanches de matière crayeuse. C'est l'assemblage des tessons de ces centaines de poteries et leur restitution qui prend, parmi le traitement du matériel archéologique de Han-sur-Lesse, une place prépondérante.

M.E.MARIËN.

L'étude du matériel en vue de sa publication en monographie est en cours.

L'exposition provisoire du matériel a donné lieu à la publication de deux catalogues d'exposition:

M.E.MARIËN, Découvertes à la Grotte de Han (Brux.1964)
ID. et L.VANHAEKE, Nouvelles découvertes à la Grotte de Han (1965

Quelques articles préliminaires:

M.E.MARIËN, Volet de diplôme militaire ~~découvert~~ trouvé à Han-sur-Lesse, Helinium IV, 1964, 52-55.

M.E.MARIËN, Rasoir romain découvert dans la grotte de Han, Helinium XI, 213-227.

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Madrid : 2-8 Octobre 1972

e Anika Skovran - Conservateur de la Galerie de Fresques à Belgrade
(Yougoslavie)

LE TRANSPORT DE L'EGLISE DU MONASTERE DE PIVA

Problèmes de méthodes et d'organisation

Introduction

Le Monastère de Piva, qui récemment encore n'était connu qu'à quel-
es rares amateurs d'art ancien et aux spécialistes qui s'aventuraient
ns les sentiers abrupts et impraticables qui y mènent, est devenu, ces
rniers temps, l'objet de l'intérêt grandissant manifesté par un public
i dépasse largement les cercles étroits des spécialistes. La raison
cet intérêt réside dans le sort étrange et assez malheureux réservé
ce monument.

A la suite de la construction du système hydroénergitique de Mratinje
devra être délogé de ses assises auprès de la source de Piva sur les-
elles il se dressait depuis le XVIe siècle et être transféré beaucoup
us haut sur un plâteau la surplombant.

Le transfert des monuments culturels s'est montré nécessaire à plu-
eurs reprises et de nos jours par suite des exigences du progrès tech-
que, non seulement en Yougoslavie mais aussi dans d'autres pays. Des
numents célèbres tels que le temple d'Abu Simbel en Egypte ou l'église
Pharos (avec ses fresques), pour ne citer que les monuments les plus
portants menacés par la construction du barrage du Nil, ou encore le
ansfert effectué récemment en Yougoslavie du Monastère de Dobricevo
r la Trebisnjica, ne constituent pas seulement un précédent, mais peu-
nt aussi nous servir de consolation car ils nous prouvent qu'il est
ssible, sous condition d'engagement suffisant de frais et d'efforts,
sauver ces précieux monuments de leur sort de destruction complète.

Si nous considérons tous les exemples de transfert de monuments
fectué ces derniers temps à l'aide des moyens techniques les plus mo-

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dernes, en particulier lors de l'exécution de l'opération la plus délicate de descente et transfert des fresques (soit que le monument même soit transféré ou seulement consolidé sur place, comme par exemple l'église Ste Sophie à Ohrid), nous sommes obligés de souligner que le transfert du Monastère de Piva constitue une tâche beaucoup plus difficile que dans tous les cas cités dépassant toutes les expériences faites chez nous ou à l'étranger.

Dans le cas du Monastère de Piva des difficultés exceptionnelles sont causées d'une part par le mauvais état de conservation du monument et d'autre part par les conditions climatiques et le manque de communications.

L'emplacement actuel reposant en partie sur l'argile, le glissement du terrain, les assises peu profondes, ayant provoqué des fissures menaçant sérieusement les murs et les fresques qui s'y trouvent, le détachement des fresques d'un intonaco de l'épaisseur minime sur les murs en pierres sont autant de facteurs qui rendent plus difficile l'opération de descente des fresques.

Dans un tel état de choses le délogement, c'est-à-dire le transfert du monument constitue une entreprise beaucoup plus difficile que s'il s'agissait de conditions normales et d'une meilleure conservation. D'autre part, pour étrange que cela puisse paraître, ce transfert pourrait, à condition d'un engagement suffisant d'experts appropriés et d'une exécution consciencieuse des travaux, prolonger l'existence de ce monument qui tombe en ruines!

Disons toutefois que ce monument pourrait résister encore pendant des siècles à condition de ne pas y toucher.

Rien n'a été publié sur ce monastère étant donné que son accès, récemment encore fort difficile, le tenait à l'écart des recherches scientifiques. Ceci constitue encore une circonstance aggravante étant donné qu'un monument d'une telle valeur qui se prépare à être démonté et délogé doit posséder avant d'être disloqué une monographie détaillée, qui, dans notre cas particulier, à la valeur spéciale de permettre la conservation du monument in situ.

II. Signification du Monastère de la Piva

Construit au XVIe siècle en un lieu sauvage très isolé, le Monastère de la Piva est un témoignage particulièrement significatif de la persistance de la vie culturelle nationale et ortodoxe au Montenegro sous l'occupation turque.

L'ensemble architectural du monastère de Piva est en relation étroite avec le cadre naturel de son paysage. Ils nous montrent les conditions difficiles imposées par la domination ottomane dans lesquelles le monastère a été édifié au prix de nombreux sacrifices. C'est ainsi que les environs du monastère, par leur austérité et la difficulté de leur accès, prennent une signification de témoignage historique qui dépasse celle de la beauté naturelle du site. C'est la raison pour laquelle il convient de conserver intact ce paysage et sa faculté d'évoquer un moment et une ambiance historiques.

D'après les inscriptions trouvées dans le naos et narthex qui représentent des documents précieux sur la construction et l'ornementation de l'église du monastère de Piva, celle-ci aurait été mise en chantier à trois reprises. Sa construction fut effectuée de 1573 à 1586, les fresques de la partie principale de l'église de 1604 à 1605, celles de la voûte du narthex aussi en 1604 et celles de ses parois en 1626.

Le fondateur métropolite Savatije a construit sa grande église en trois nefs sur l'emplacement d'une ancienne église dédiée, elle aussi, à la Dormition de la Vierge. Cette église qui précéda l'actuelle église monumentale construite par Savatije nous est restée inconnue et devait probablement se trouver en ruines. Ceci nous est témoigné par certains vestiges et par des documents historiques. Dans la partie inférieure des murs de l'église se trouvent incorporés de grands blocs de pierre utilisés auparavant et qui semblent, d'après la manière dont ils sont façonnés, avoir été des pierres tombales. Une inscription datant de 1568 et qui se trouve sur le Triode faisant partie, avec d'autres livres et vêtements liturgiques du legs de Savatije à : "la sainte communauté monacale de la Dormition de notre très sainte reine céleste Mère de Dieu et Vierge Marie, sise au monastère auprès des sources de la Piva...", de même qu'une autre inscription datant de 1572 et dans laquelle l'on mentione Visarion, métropolite de Raška, Novi Pazar et Stari Vlah, comme donateur d'un psautier à la même église, nous montrent qu'il devait y avoir certainement avant 1573 une autre église sur le même emplacement, étant donné que les deux legs ont été faits avant la fondation de la présente église.

Le monastère actuel a été construit bientôt après la restauration de la patriarchie de Pec sous le patriarche Makarije, frère du Grand vizir Mehmed Sokolovic. Ce n'est que durant les conditions favorables qui régnaient sous le vizirat de ce Grand Vizir d'origine chrétienne, que pût être construite dans une région relativement libre comme l'était celle des Drobnjaks et de Piva, au milieu de l'asservissement général de la péninsule balkanique sous le joug ottoman,

et grâce à l'engagement patriotique du donateur et de la communauté des moines, une oeuvre aussi monumentale. L'église de Savatije, à trois nefs dans l'enceinte du monastère de Piva était destinée à devenir, à côté du monastère de Moraca, un centre culturel d'importance primordiale de la région d'Herzégovine et du Monténegro. A cette époque les métropolites influents d'Herzégovine réussirent à obtenir l'autorisation de rénover ou construire de nombreuses églises grâce aux postes importants que leurs compatriotes occupaient auprès de la Grande Porte. Par un décret du sultant il avait été interdit aux Serbes de construire de nouvelles églises, mais comme la restauration des anciennes avait été autorisée, c'est sous le couvert de celle-ci qu'ils entreprirent de construire à l'emplacement des vieilles églises qui tombaient en ruines, des églises nouvelles, parfois plus grandes que l'ancienne, comme cela avait été le cas de l'église de Piva.

Les fresques du monastère de Piva constituent l'ensemble le plus vaste et certainement l'un des plus importants de la peinture murale exécutée dans les Balkans dans la période post-byzantine.

Le groupe de peintres qui de 1604 à 1605 exécuta les fresques de l'église principale du monastère de Piva n'était pas un groupe homogène quand à la qualité artistique de leurs travaux, mais ils ont réalisé un ensemble iconographique à teneur excessivement riche inspirée en grande partie par l'influence de l'art crétois de l'époque.

Kir Siméon, igoumène du monastère de Piva qui s'occupait de la peinture murale, se rendit au Mont Athos avant de faire peindre les murs de l'église et même plus tard au cours des dix ans de son administration abbatiale du monastère, il entretient, jusqu'à sa mort, des liaisons étroites avec le Mont Athos, y envoyant ses moines pour y copier des livres liturgiques destinés à l'église de Piva. Il est certain que ce moine cultivé et entreprenant, au temps duquel un atelier de copistes avait été ouvert au sein du monastère, avait exercé son influence sur le choix des sujets iconographiques devant orner les murs du naos de l'église de Piva.

Des sujets d'envergure, enclyclopédique enrichis par des motifs iconographiques rares et remarquablement circonstanciés distinguent cette peinture aux dimensions monumentales mais de valeur artistique inégale. Le répertoire des fresques du naos de Piva se distingue par sa grande richesse. Dans la conque de l'abside se trouve une immense Vierge nommée Platitera sous laquelle défilent la liturgie céleste, la communion des apôtres, l'Adoration de l'Agneau et un imposant cortège des pères de l'église, tandis que dans le naos sont représentés, en plus des cycles habituels des grandes fêtes et de la Passion du Christ traités en détail, des scènes évoquant les miracles du Christ et des scènes de la vie de la Vierge, de St. Jean et d'autres

saints et, ce qui est plus rare, l'origine des prières: "O tebe radujetsja" (Hosanna) et "Jerusalim" (Jérusalem). Ces scènes représentent la viste aux lieux saints de la Vierge Jérusalem, Bethleem et Nazareth après la résurrection du Christ. Cette composition, tirée de la "Legenda aurea" est fort rarement illustrée par des fresques. La composition avec le fondateur faisant à la Vierge l'offrande de l'église se trouve près du portail sud.

La valeur artistique de cette peinture murale est variable et l'on peut en conclure que l'art et la culture des membres du groupe de peintres qui la réalisa et s'en fut plus tard peindre en 1608 les murs de l'église de Hopovo en Syrmie l'étaient aussi.

Un dessin sec, un coloris assez cru mais pur et la simplicité du traitement pictural qui parfois se permet certaines rudesses dans le détail - toutes ces particularités (qualités ou défauts) de cette peinture se noient dans une impression générale de multitude et d'ampleur des sujets iconographiques qui se déroulent sur les immenses parois des murs. La technique du procédé utilisé montre la maîtrise des peintres qui connaissaient bien leur métier et savaient couvrir rapidement de peinture d'immenses surfaces murales. La réalisation picturale de certains sujets iconographiques montre que les maîtres en question connaissaient bien les fameuses oeuvres contemporaines exécutées dans les célébres monastère du Mont Athos, par exemple dans la Lavra. A en juger d'après le mélange de textes grecs et serbes sur les philactères que portent les prophètes représentés dans les zones supérieures, on est appelé à présumer que se groupe de peintres était formé de Grecs et de Serbes.

Pendant que les fresques du naos de l'église de Piva se distinguent par la multitude de leurs sujets iconographiques, celles du narthex ont pour nous une valeur particulière car elles proviennent du pinceau de maîtres appartenant à la population autochtone, à savoir du pope Strahinja de Budimlje et de Kir Kosma.

La peinture du narthex, comme nous le dit une inscription brève au-dessus de la fenêtre du mur septentrional, a aussi été entreprise en 1604, du temps de l'igoumène Siméon. L'on doit au pinceau de Strahinja les deux zones supérieures du narthex qui englobent une partie de l'illustration de l'Hymne Acathiste (du premier icos au huitième condacos) la plus grande partie des Conciles éucuméniques (du troisième au septième), quelques scènes de la Vie des apôtres se rapportant à Saint Pierre et Saint Paul et l'illustration de la parabole du Bon Samaritain, comme aussi une série de

médaillons avec des bustes de saints sur le cintre des arcs reliant les pilastres.

De toute l'oeuvre de Strahinja, qui se distingue par la fraîcheur naîve de la narration, ce sont les fresques du narthex de Piva et en particulier les scènes de l'Acathiste de la Vierge, qui atteignent le sommet de sa création artistique. Ces oeuvres peuvent être comparées par la fraîcheur de leur narration aux scènes des miracles des Apôtres sur la grande icône de l'Archange Michel du monastère de Moraca datant de 1600. Les particularités bien connues de la peinture de Strahinja, son dessin schématique peu soigné, ses figures peintes à plat dont les formes sont sciemment négligées par le peintre, les traits simplifiés des physionomies qui se répètent et une certaine rigidité dans les attitudes, tout en étant présentes sur les fresques du monastère de Piva, ou plutôt dans les scènes de l'Acathiste, ne sont plus ressenties comme des défauts, étant donné que Strahinja a réussi à nous narrer les événements d'une manière inspirée, enthousiaste et sincère, comme un enfant. Son coloris est franc et les coulisses dans lesquelles les scènes se déroulent font preuve de fantaisie. S'il lui arrive de peindre son propre entourage, par exemple les pâtres de la Naissance du Christ (quatrième icos), les petits chevaux de montagne apparaissant dans l'Adoration des Mages (cinquième condacos) ou dans la Fuite en Egypte (sixième icos de l'Acathiste de la Vierge) ou les nasses à poissons dans la scène de la Vie des Apôtres où le Christ invite Pierre et Paul à le suivre, Strahinja s'évertue à peindre le moindre détail (tel le harnais en laine multicolore des chevaux) et ce sont ces détails qui, sur ses fresques, sont les plus suggestifs et les plus beaux. Le procédé technique de la peinture à fresco est aussi beaucoup plus soigné dans le narthex du monastère de Piva que dans les autres oeuvres de Strahinja.

La peinture murale du narthex du monastère de Piva, commencée par Strahinja, fut reprise vingt-deux années plus tard, en 1626, par maître Cosme. S'insérant remarquablement bien dans l'oeuvre commencée, ce peintre continue le programme iconographique amorcé et interrompu, Dieu sait pourquoi, vingt-deux ans plus tôt. C'est ainsi qu'au temps de l'igoumène Avram et du voïvode Pavle Dragicevic fut terminée la peinture murale de l'église du monastère de Piva commencée du temps de l'igoumène Siméon.

Le nom du zographe Kir Cosme est le nom le plus célèbre parmi les peintres de l'époque.

Les particularités du style de ce peintre de talent sont très marquées, si bien que l'on peut reconnaître ses oeuvres même si elles ne sont pas signées.

En plus des fresques du narthex du monastère de Piva datant de 1626, maître Cosme travailla aussi à la peinture de l'iconostase datant de 1638-1639. Les icones de maître Cosme se trouvant à Piva, et parmi lesquelles se distinguent par leur beauté celles de la Dormition de la Vierge et celle de Saint Georges, sont antérieures à ses oeuvres du monastère de Moraca qui sont sa réalisation la plus vaste.

Les fresques de maître Cosme se trouvant dans le narthex de l'église du monastère de Piva constituent du point de vue iconographique et artistique des réalisations de grande valeur. Adoptant le programme de décoration tracé par Strahinja, Cosme continue, un quart de siècle plus tard, à reproduire dans on langage pictural exceptionnel, les strophes des icos et condacos de l'Acathiste de la Vierge. C'est de même que s'insérant parfaitement dans le schéma de la répartition des fresques, il continue à peindre les autres cycles.

La science iconographique exceptionnelle de maître Cosme nous apparaît aussi dans le choix d'autres sujets compliqués, très en faveur dans les milieux théologiques du Mont Athos. Maître Cosme connaissait évidement parfaitement la peinture crétoise qu'il avait eu l'occasion de rencontrer au Mont Athos. Quoique nous n'ayons aucun renseignement sur sa formation et ses déplacements, au point que l'on [illegible] se donner beaucoup de mal pour connaître son nom et qu'on ne l'adopte encore qu'avec réserve, on peut se fier à sa peinture comme à une source certaine. Cette peinture est heureusement très explicite. A en juger d'après sa facture, sa palette claire et brillante, son dessin adroit, élégant et sûr dont la beauté se voit le mieux dans les gestes des mains, la chute draperies et l'attitude des personnages dans les compositions réalisées avec une bonne connaissance des lois de la perspective, comme aussi d'après le modelé soigné de ses formes, la pastosité de ses couleurs et les inscriptions aux caractères cyrilliques élancés d'une grande beauté dans la langue choisie -

maître Cosme a dû avoir été formé à bonne école dans les meilleures traditions de la peinture serbe du XIVe siècle tout en étant parfaitement au courant, des réalisations artistiques et des conceptions théologiques du monde orthodoxe contemporain par l'intermédiaire du Mont Athos qui, à l'époque, était un facteur important de l'unité religieuse et culturelle de la chrétienneté orientale, asservie par les Ottomans.

Le fait que le Monastère a conservé tout son mobilier de la même époque que l'architecture et les fresques - l'iconostase, icônes, roue de la Vierge, porte du Narthex (ornée par incrustation), bibliothèque et trésor riche en orfèvrerie, lui donne une valeur toute particulière. De tels ensembles, qui conservent l'image complète d'une époque déterminée, sont très rares , et sont seuls susceptibles de transmettre l'impression originale produite par le monument "vivant".

III. Situation géographique et climat

Le monastère de Piva est situé dans la partie oontinentale du Monténegro, dans une région de hautes montagnes entrecoupées par les gorges profondes de ses cours d'eau. C'est au début de l'une de ses gorges, à l'endroit où la Piva prend sa source, nommé Sinjac, et qui représente en réalité un phénomène unique - une espèce de lac dont l'eau surgit en grande quantité - que se trouve le monastère.

Le monastère est situé sur la peinte du ravin à une altitude de 600 mètres. Dans son entourage se trouvent les contreforts du massif central du Monténegro formé par les sommets de Golija, Vojnik, Piva et Durmitor qui s'élèvent au-dessus de 2.500 mètres.

Cette situation géographique confère au monastère, situé sur la côte relativement la plus basse du massif montagneux, à l'endroit où celui-ci est coupé du nord au sud (approximativement) par la gorge étroite et profonde de la Piva, un climat très spécial.

La grande diversité orographique de ces régions entraîne aussi une grande diversité de climat. Dans un espace très restreint l'on constate de grandes différences de micro-climat. Pendant que dans certaines parties de ce territoire règne un climat spécifique de haute montagne il s'y trouve de petites oasis avec un climat très spécial. C'est justement dans l'une de ces oasis que se trouve

le monastère. Pendant qu'en hiver un froid glacial règne dans ses environs, la température est relativement élevé dans ses proches alentours. Cependant le caractère spécifique de ce terrain provoque aussi quelques anomalies. Il arrive, en certaines nuits claires d'hiver, que la température auprès du monastère est sensiblement plus basse que sur d'autres terrains élevés même à plus de 500 mètres au-dessus du monastère. Ce sont là des inversions de température fortement prononcées qui arrivent à leur culmination aux heures avancées de la matinée lorsque le soleil tombe à pic sur les terrains horizontaux éloignés à peine d'un kilomètre. Une autre caractéristique est le vent chaud (Foehn) qui élève sensiblement la température et diminue l'humidité relative de l'atmosphère, Tout cela entraîne des variations énormes de température, d'humidité et de direction du vent, très caractéristiques.

Les grandes amplitudes atteintes dans un intervalle de temps très restreint exigent par suite de l'obligation de transférer le monastère, une étude approfondie de ces phénomènes précédée de mensurations précises et appropriées.

Les mensurations effectuées jusqu'à présent montrent le bien fondé de ces exigences. Elles ont permis de constater des fluctuations très grandes dans l'humidité et la température de l'air au cours du mois relativement sec de mars 1972. Pendant 15 jours consécutifs (sauf 3 exceptions) l'humidité se tenait régulièrement à 7 heures du matin aux environs de 95, voire 100%. De ce maximum elle diminue rapidement pour arriver vers 14 heures à son minimum absolu de moins de 20%, ce qui est le propre d'un air très sec.

On a donc, au cours d'une même journée, un air très humide et un air très sec. La date du 20 mars 1972 en est un exemple frappant. Vers 6 heures du matin l'hygrographe pointait exactement sur 100% d'humidité, pour tomber, huit heures plus tard à seulement 7%. Amplitude invraisemblable dans un intervalle si court. Mentionnons aussi que l'apparition d'une humidité si basse est exceptionnelle (sans égard au fait que les valeurs n'ont pas été corrigées), et que de telles variations au cours d'une seule journée sont presque inconnues.

La température suivait aussi un cours régulier. Le minimum était atteint une heure avant le maximum d'humidité et le maximum une heure après le minimum d'humidité. Pendant la plupart des journées de la période mentionnée elle se tenait au matin au-des-

sous de 0° centigrade, pour atteindre au milieu de la journée (de 14 à 15 heures) même 20 degrés. Le termographe marquait le 20 mars 1972 vers 6 heures du matin moins 2 degrés centigrade et vers 14 heures trente, plus 20 degrés, ce qui constitue une différence énorme de 22 degrés.

La situation concernant la direction du vent est semblable. Il est presqu'impossible de la déterminer. Les aspérités du terrain caractérisé par la gorge profonde à l'est du monastère qui va du sud au nord, conditionne une modification sensible des vents sans égard au sens dans lequel ils soufflaient originairement. Il y a d'ailleurs des moments pendant lesquels l'on ne remarque aucun souffle de l'air parce que le terrain se trouve dans un trou.

Ces quelques exemples montrent la situation climatique très délicate dans laquelle se trouve le monastère. Les vieilles chroniques parlent déjà des vicissitudes météorologiques du lieu. Et il est probable que l'on a entrepris jadis sur la foi des annotations faites par les moines, des mesures de protection, ce qui explique en quelque sorte la condition relativement bonne dans laquelle se trouvent les fresques et les icones.

IV. Etudes préparatoires

Projet d'étude de déplacement du monastère de Piva est fait en coopération des divers spécialistes - historien d'art, archéologue, architecte, staticien, peintre-restaurateur, chimiste, météorologue, ingénieur-forestier (pour la replantation des arbres faisant partie de l'ambiance).

Les études préparatoires étendues sur l'architecture et des peintures (fresques, l'iconostase et icônes) lesquelles ont été effectuées - étaient très favorablement apprécié par les membres de la commission des spécialistes chargée de l'étude du déplacement du monastère de la Piva (N. Martinovic, A. Deroko, H. Plenderleith, J. Zdravkovic, P. Philippot, V. Djwic, Z. Blasic, etc.).

Lors de la rédaction de l'étude élaborée à cet effet (documentation sur 1.300 m2 de fresques) nous avons recourru à une méthode peu habituelle d'exposition des matériaux scientifiques, et documentaires sur les particularités du monument, la teneur iconographique des fresques, l'état de leur conservation et les

dégâts survenus sur les fresques et les autres objets d'art. Dans le désir d'éviter les longs textes descriptifs et narratifs qui ne nous semblent pas suffisamment clairs, nous avons présenté les résultats de nos recherches exécutées avec un maximum de précision d'une manière qui donne une vue d'ensemble. Nous nous sommes efforcés d'enregistrer de façon objective tous les renseignements offerts par le monument et de les présenter de façon moderne.

Etant donné qu'il s'agit de peinture,notamment du riche répertoire iconographique du monastère de Piva,nous avons recouru à la méthode visuelle de présentation de sa teneur et du degré de sa conservation.Tenant compte du fait que le monastère devra etre délogé, donc disloqué et que son ornement principal,sa peinture murale devra être enlevé,il nous semble indispensable et inévitable de recourir à la documentation visuelle tout en insistant sur l'élaboration d'un schema de la répartition des fresques sur la surface deployée des murs en les dessinant à une échelle fixée et constante,et marquant le degré et le genre d'endommagement des surfaces murales et en les photographiant en totalité.Lors de la descente des fresques certaines de leurs parties doivent être inévitablement détruites,aussi considerons-nous de notre devoir primordial de noter de facon aussi objective que possible l'état des fresques dans le moment de l'enlevement,pour les arracher ainsi à l'oubli.

Une documentation volumineuse traitant du monument est un auxiliaire précieux dans l'oeuvre de transfert de l'église. C'est de la précision de cette documentation que dépendra en grande mesure le succès de la reconstruction de l'ensemble architectural du monastère et de la remise en place des fresques.

V. Transport et calendrie des operations

Le problème du transport du monastère de la Piva se distingue d'operations analogues realisées dans le passé par le grande complexité des opérations,qui concernent à la fois le complexe architectural,les fresques (1.300m^2) et le mobilier monumental (iconostase 9m du hauteur).

Ces circonstances rendent particulièrement indispensable une planification détaillée des opérations,comte tenu de leur interdépendence, du temps disponible avant la montée des eaux et du fait que le climat de Piva ne permet guère de travailler plus de 6 mois par an.

Il est évident que le souci principal est de conserver,dans les opérations de déplacement et de remontage,le caractère d'authenticité de l'oeuvre.

Choix du nouveau site est satisfaisant et tant que possible analogue au site original.

Pour sauvegarder l'authenticité du complexe architectural,il est essentiel de conserver aussi rigureusement que possible les relations originales entre les divers éllements: église,habitation,murs, porche,four et tombeaux.

La dépose des fresques est étroitement coordonnée avec le demontage de l'architecture.

La transposition des fresques est fait de maniere de respecter scrupuleusement les irrégularités de surface et les caractéristiques de texture qui révélent l'unité de la peinture et de l'architecture. Techniquement,on a procédé la dépose par stacco avec l'intonaco partout ou cétte operation etait réalisable.Malgré le fait que le mortier soit tombé à bien des endroits par suite de sa mauvaise condition et couche très mince,l'application du système stacco était préférable car il permettait de mieux garder les irrégularités de la surface qui n'aurait été possible avec le procédé de strapo.
L'opération de strappo on a fait dans le narthex - seulement quelques exemples - pour pouvoir sauver quelques sinopie lesquels on a pu constater partout dans le narthex.

L'enlèvement des fresques a été exécuté de facon classique,à la colletta,ce qui a donné des résultats excellents.L'on a tenté aussi le système d'enlèvement au moyen des nouveaux matériaux plastiques - " rivil",ce qui,à plusieurs point de vue n'était pas satisfaisant (manque d'expérience,quantité des fresques,langueur du procédé etc.)

Un système approprié de calorifères et de ventilateurs a permis le conditionnement climatique nécessaire.

Lors de l'enlèvement des fresques de toutes les surfaces courbes l'on s'est servi d'un système de moulage,pendant que pour les surfaces planes l'on s'est servi d'un système nouveau de lattes amovibles fixées en rangées sur toile.Ce système facilite le contrôle au cour des travaux.

L'église même pour le moment sert comme dépôt le plus convenable des fresques détachées.Les fresques y resteront jausqu'au le printemps 1973,moment du démontage de l'architecture.Le dépôt des fresques dans un abri en attendant le séchage complet de la nouvelle construction est essentiel.L'entrepasage des fresques détachées inplique des précautions particulières (Car la colle animale utilisée pour le facing

du stacco est très sensible aux moississures).

Sur le nouveau site les bâtiments du monastere (habitations) sont déjà construites et lorsque la construction sera suffisamment sèche les fresques seront y transportées.

Dans le cadre de notre projet d'exécution des travaux de deplacement du monastère de Piva (voir en annexe), nous désirons encore une fois insister sur l'importance de respecter le rythme et les termes de réalisation des phases prévues pour ces travaux. Le temps dont nous disposons est excessivement court, si bien qu'il faut l'utiliser rationellement. Il s'agit de bien synchroniser les travaux pour ne pas avoir à forcer le rythme ce qui serait inadmissible dans ce genre de travail.

Le processus extrêmement délicat de descente des 1.300m^2 des fresques avait exigé une suite graduelle des travaux et l'écoulement d'un temps précis qui ne peut être abbrégé sans que cela se reflète négativement sur la qualité du travail.

Nous sommes heureux de pouvoir constater que cette première et importante partie des travaux a été terminé (en 1971, 1972) à notre grande satisfaction.

Pendant toute la durée des travaux d'enlevement des fresques, nous avons eu le bonheur de bénéficier des consultations des éminents specialistes Mr et Mme Paulo et Laura Mora.

VI - Problèmes d'organisation

L'organisation administrative de l'entreprise de déplacement du monastère de Piva a été confiée au Service pour la protection des monuments historiques du Montenegro.

Etant donné la complexité des opérations à organiser, et la nécessité de les coordonner techniquement et chronologiquement, il été essentiel d'assurer, au niveau de la direction, une étroite collaboration entre les divers secteurs et particulièrement entre les responsables de l'architecture, de la restauration des fresques et des objets mobiliers, et l'historien de l'art chargé de veiller au respect des exigences esthétiques et historiques.

Il faudra également tenir compte du fait que le coût des opérations ne peut être établi avec exactitude à l'avance. La durée de séchage des constructions ne peut être prévue avec précision, et le

coût de certaines opérations pourra varier sur une période aussi longue que quatre ou cinq ans.

Les meilleurs restaurateurs de Yougoslavie ont pris part à ces travaux.Ils formaient un noyau autour duquel se groupaient de jeunes restaurateurs et étudiants à raison de cinq jeunes autour d'un expert. Ceci leur servira d'école pratique de grande valeur pour leur carrière future.

L'organisation du chantier dans la situation reculée du site exiga d'assurer l'alimentation du chantier en eau et en courant électrique, et aussi d'assurer les moyens d'existence d'une equipe de soixante personnes.

VII - Documentation

En plus de la documentation de l'état du monument avant son déplacement,on a constitué une documentation des opérations de déplacement,en tenant compte de deux points de vue:

1. la nécessité de documenter l'intervention sur le monument,notamment en vue d'interventions futures,

2. l'intérêt considérable de l'opération du point de vue méthodologique,qui lui donne une valeur exemplaire.

Signalons encore que l'on est en train de tourner un film documentaire sur le transfert du monasrère,si bien que toutes phases des travaux seront fixées sur pellicule.

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The International Council of
Museums -
Committee for Conservation

Conseil International des
Musées -
Comité pour la Conservation

Madrid : 2-8 octobre 1972

André Bouscaras : (~~Coordinateur~~)

L'épave des bronzes de Rochelongues.

Du Delta du Rhône aux premiers contreforts des Pyrénées, la côte du Languedoc-Rousillon, dans le Sud de la France est basse, bordée d'étangs séparés de la mer par seulement un cordon littoral, parfois très étroit.

Cette zone, sans abris naturels, est balayée par des vents violents, soufflant surtout de deux directions: W - NW et S.E.

Seules, quelques collines romptent la monotonie de cette côte plate et pouvaient éventuellement procurer un abri aux navigateurs dans l'antiquité et ce, jusqu'à une époque où la maniabilité des embarcations les a rendu plus aptes à affronter les sautes de vent.

Du Sud au Nord, ces abris naturels sont : la colline de Leucate, en Roussillon; légèrement plus au Nord, les trois îles fermant jadis l'ancien Delta de l'Aude avant qu'il ne soit colmaté par les alluvions de ce fleuve; à l'embouchure du fleuve Hérault, le cône de scories volcaniques du Mont Saint Loup qui culmine à III m., prolongé vers le Sud-Est par une coulée de basalte qui forme une falaise dominant la mer et au large l'îlot de Brescou; environ trente kilomètres plus au Nord, le Mont Saint Clair qui domine le port actuel de Sète.

Parmi ces accidents du relief, seules les îles fermant le Delta de l'Aude et le massif volcanique d'Agde offraient vraiment un abri important et un mouillage sûr.

C'est donc surtout vers ces deux points que les navires antiques convergeaient en cas de mauvais temps sans toutefois y parvenir toujours.

De plus, ces deux fleuves côtiers, Aude et Hérault autrefois naviguables sur une portion importante de leur cours, traversent de vastes régions fertiles où la densité des habitats était relativement importante dans l'antiquité et attiraient

vraisemblablement les navigateurs-commerçants en mal de trouver des clients pour écouler leurs marchandises.

Dès 1949, nous nous sommes intéressés aux fonds sous-marins d'Agde et dûment munis d'une autorisation de Recherches Archéologiques, nous n'avons pas tardé à découvrir de nombreuses traces du commerce maritime antique. Traces constituées, soit par des gisements homogènes, plus ou moins importants, provenant de naufrages; soit par des objets isolés jetés à la mer ou perdus accidentellement, toutefois intéressants par ce qu'indiquant un mouillage ou une route commerciale.

Mais la découverte la plus spectaculaire par la nature et l'importance du mobilier remonté fût celle effectuée en 1964.

Le 24 juillet de cette année-là, accompagné de deux autres plongeurs j'avais décidé de prospecter un banc de roches et de posidonies situé face aux deux pointes rocheuses de ROCHELONGUES, à 500 m. au large et à une profondeur de 6 à 7 mètres.

En effet, il est toujours très intéressant de repasser chaque année la bordure des bancs rocheux : car les tempêtes d'hiver, à si faible profondeur, ne manquent pas d'y dégager chaque année de nouveaux objets.

Je devais moi-même, suivre les bords du banc, alors que mes amis, décalés de 10 en 10 m. , devaient balayer une zone située plus vers l'intérieur.

La plongée avait débutée depuis quelques minutes à peine quand mon regard fût arrêté par deux objets vert-de-grisés émergeant partiellement du sable qui emplissait une faille entre deux roches.

Les ayant dégagés, j'eu la surprise de constater qu'il s'agissait d'un lingot de cuivre et d'une hache douille quadrangulaire.

Un sondage effectué aussitôt dans la faille, me donna très rapidement d'autres objets: encore des lingots et des haches, mais aussi anneaux, bracelets, boutons et pendentifs.

C'est ainsi que débuta la fouille de l'Epave des Bronzes de ROCHELONGUES.

Elle s'est poursuivie pendant plusieurs années de 1964
à 1971, à raison de deux mois de travail par an : juillet et
oût, et ce tous les jours où le temps le permettait.

Cette fouille menée en plein accord avec la Direction des
echerches Archéologiques sous-marines, fût effectuée uniquement
ar des plongeurs bénévoles exerçant dans la vie des professions
rès diverses : technicien radio., menuisier, assureur, chef d'en-
reprises, étudiant, ouvrier, etc....

Les subventions qui nous ont été accordée soit par le Mi-
istère des Affaires Culturelles, soit par le Conseil Général de
'Hérault, ne parvenaient que rarement à couvrir nos frais pourtant
alculés au plus juste : achat et entretien du matériel de plongée,
hotos, tirage de plans, etc.....

Les embarcations servant à la fouille étaient souvent bri-
olées: réservoirs larguables de bout d'ailes d'avion, moteur
rovenant des surplus américains, barge de débarquement réformée
tc..... même les appareils de plongées étaient fabriqués en par-
ant de bouteilles rééprouvées de la Kriegsmarine. Question maté-
iel, ce fût donc une improvisation d'un bout à l'autre.

Seules quelques interventions de l'Archéonaute, après sa
ise en service, nous ont permis de travailler avec des moyens
echniques modernes. Nous en reparlerons plus tard.

Au cours de la campagne de fouille 1971, nous avons acquis
a quasi-certitude que le gisement était épuisé. Il nous avait
onné au cours de 600 heures de travail au fond 1700 objets de
ronze et 800 kgs de culots de cuivre.

Ce résultat fût obtenu, non sans mal, car, le milieu, les
onditions de travail et les objets que nous étions appelés à dé-
ouvrir nous posaient des problèmes parfois assez difficilesà ré-
oudre.

Si la faible profondeur était dans un sens un avantage, car
lle nous dégaeait de toute inquiétude quant au temps de plongée
t aux paliers éventuels de décompression, elle offrait aussi de
érieux désagréments : pillage relativement facile, dès que la
écouverte fût connue, ce qui nous obligea à une surveillance sans
elache, et aussi répercussion rapide au fond des mouvements de
urface de la mer, ce qui avait pour inconvénient de troubler

rapidement les eaux, nous obligeant à interrompre le travail assez fréquemment.

Nous devions aussi tenir compte de la topographie du fond pour organiser le chantier.

Comme nous l'avons indiqué précédemment, ce fond est constitué d'un herbier de posidonies, coupé de clairs de sable d'où émergent parfois le substrata basaltique avec des boules de basalte provenant de son altération.

Si dans le sable, le dévasage était relativement facile, il n'en n'était pas de même quand nous devions fouillé dans l'herbier de posidonies. Il nous fallait au préalable les arracher et les évacuer en dehors du gisement. Les roches parfois volumineuses ne faisant pas corps avec le sous-sol, devaient être déplacées à l'aide de leviers afin de pouvoir dégager les objets se trouvant au-dessous.

Aucun moyen mécanique de dévasage n'étant à notre disposition, du moins pendant les quatre premières années, tout le travail dût être effectué à la main (heureusement, la main d'oeuvre était gratuite) et dans un sens, ce fût une bonne chose, car si certains objets étaient relativement volumineux : haches, bracelets, pointe de lance et lingots, d'autres ne pesaient parfois qu'un quart de gramme : perles, boutons, etc...... et par un dévasage mécanique ils auraient été déplacés, peut-être même définitivement perdus.

Par contre, la méthode de dévasage à la main que nous avons adoptée, quoique lente, permettait un travail beaucoup plus précis. Elle consistait, par un mouvement de va et vient de la main, à créer un courant d'eau qui entrainait les matières les moins denses : sable, vase et coquillage laissant en place les objets métalliques d'une densité supérieure.

Toutefois, pour travailler en eau toujours claire, nous devions tenir compte du sens du courant variant fréquemment au fond en fonction des vents, nous obligeant parfois à changer l'orientation de la recherche au cours d'une même plongée.

De plus, deux ou trois plongeurs au maximum pouvaient travailler en même temps au fond afin de conserver une eau relativement limpide.

En 1968, 70 et 71, la venue de l'Archéonaute, navire spécialisé dans la Recherche Archéologique sous-marine, équipé de tous les moyens modernes de dévasage nous a permis la fouille de zones très ensablées (plus de 1m20 de sable).

Nous connaissions alors parfaitement la topographie du gisement, et avons pu effectuer ce dévasage dans des secteurs où nous étions pratiquement certains de ne rencontrer que des lingots et où il n'existait donc aucun risque de déplacer de petits objets. Cette fouille a confirmé nos prévisions, seuls des lingots plus ou moins volumineux furent dégagés.

Comme nous l'avons précédemment indiqué, les risques de pillage et l'impossibilité d'évacuer au lin les déblais, nous ont interdit de dégager en une seule fois une partie importante du gisement. Ainsi, aussitôt qu'un demi mètre carré de surface était dégagé ou qu'une faille était désensablée et au plus après chaque demi-journée de travail, nous devions remonter le mobilier découvert, non sans l'avoir au préalable photographié et situé par triangulation par rapport à des roches caractéristiques émergeant de l'herbier.

Ces positions étaient aussitôt reportées sur un plan. Nous avons ainsi pu constater que les objets les plus lourds, les moins usés par l'abrasion du sable étaient situés dans la partie Sud-Est du gisement. Tout le mobilier dans cette zone se trouvait directement au contact de la roche basaltique, sans aucune stratigraphie apparente. Des objets beaucoup plus récents: deux monnaies de Constantin, ainsi que des balles de fusil de la dernière guerre étaient mélées au mobilier antique, ce qui prouve que les objets métalliques de densité élevée ont peu à peu traversé la couche de sable très flüide et ont été arrêtés par la roche.

De plus, étant donné la faible profondeur et les tempêtes violantes, il est probable qu'une partie importante du mobilier a été à plusieurs reprises totalement dégagée, ce qui explique et l'usure due au frottement du sable constaté sur bon nombre d'objets et la dispersion du mobilier, car partant du point de grande densité, situé au Sud-Est du gisement, dont nous avons précédemment parlé, les objets sont dispersés en éventail en direction N.W. (les tempêtes dominantes venant du Sud-Est).

Plus nous nous éloignons de l'extrêmité du Sud-Est du gi-
ement, plus les objets sont de taille réduite et plus ils ont
sés par l'abrasion du sable. A la limite N-W, certains objets
éplacés relativement récemment, quoique situés sous l'herbier de
osidonies, ne se trouvent plus sur la couche de roche formant le
ubstrata mais en position intermédiaire entre la surface et cette
ouche.

Il semblerait au premier abord qu'étant donné cette disper-
ion, on ne puisse recueillir aucune indication sur le groupement
u mobilier au moment de son immersion. Il n'en est heureusement
ien; car si nous nous rapportons au journal de fouilles et à la
osition des objets au fond qui apparait nettement sur le plan,
ous constatons qu'ils sont très souvent groupés par variétés.

Il n'était pas rare en cours de fouille de rencontrer en
n même point une vingtaine de haches ou autant de bracelets; une
ibule est rarement découverte seule, mais presque toujours
ccompagnée de quelques autres. Quand nous découvrions un burin
u un marteau, nous étions pratiquement certains de trouver quel-
ues objets semblables à proximité.

La dispersion a donc eu lieu au départ par groupes d'objets
emblables ce qui parait indiquer que le mobilier, lors de son
mmersion, était rangé par catégorie, probablement dans des sacs.
uelques objets absolument semblables, fondus dans le même moule:
endentif ou anneau, étaient encore réunis par des fils de cuivre.

La fouille actuellement terminée, nous pouvons dresser un
apide inventaire de tout le mobilier recueilli, car il n'entre
as dans le cadre de cette étude d'en entreprendre une description
étaillée.

Les armes : pointes de lances, de javelots et de flèches
ont peu nombreuses. Quelques fragments d'épée et de poignard à
oie plate à deux rivets ont été également retrouvés.

Par contre, les pièces de harnachement sont assez abondantes:
randes appliques, boutons à quatre pieds, éléments de mors etc...

Les haches, elles, sont très abondantes, plus de deux cents.
es plus nombreuses étant à douille quadrangulaire, quelques unes
douille ronde avec anneau de fixation; trois seulement à ailerons
erminaux.

Mais le gros du mobilier est constitué par les objets de parure: bracelets ouverts ou fermés, ronds ou ovales, quelques uns finement incisés de dessins géométriques; les bracelets dentelés ou à godrons sont également abondants.

Les annéeaux, les boutons sont très nombreux et de dimensions diverses.

Les boucles de ceinturons, à l'exception de trois qui sont rectangulaires, sont toutes en forme de croix d'Agadès, pleines ou ajourées mais ne comportant qu'un seul crochet.

Parmi les fibules, la plupart sont à double ressort et rappelle les modèles rencontrés dans les nécropoles à incinération du 1er Age du Fer en Catalogne Espagnole. Mais c'est surtout dans les pendentifs que l'on trouve une grande diversité : pendentifs triangulaires classiques ou en forme de décapsuleur, pendentifs creux, pendentifs en forme de cage, roues solaires traitées de diverses façons, pendentifs à chainette et à glands, d'inspiration très diverses.

Un collier formé d'anneaux ronds et ovales alternés est un des objets le plus spectaculaire.

Il faut ajouter à tout cela des jets de fonte ou masselottes de fusion et une série impressionnante de burins à douille et de marteaux à douille également (Ces derniers objets pourraient aussi bien être des têtes de burin, la partie médiane étant constitué par du bois).

Nous avons déjà mentionné les 800 Kgs de lingots de cuivre récupérés. Ces derniers en forme de galette plan convexe ont des poids très irréguliers, allant de 1 à plus de 6 kgs.

Ils sont en cuivre pur à plus de 99 %. Ils ont pû être obtenus soit en partant de nodules de cuivre pur, soit par fusion d'objets récupérés; dans ce dernier cas, l'étain que contenait le métal se serait volatilisé lors de la deuxième fusion.

Tout le mobilier provenant de l'Epave des Bronzes de ROCHELONGUES a été ou va être l'objet d'un traitement de conservation au Laboratoire du Fort St Jean à Marseille, dont Monsieur Jean BOUIS, que je tiens ici à remercier pour son énorme travail, est le Reponsable, mieux même l'animateur.

Des prélèvements de métal en vue d'analyses ont été effectués sur presque tous les objets par les assistants du Professeur Junghans du Musée de Stuttgart.

Les dessins de tous les objets caractéristiques qui devraient figurer dans la Publication définitive du gisement sont dûs à MM. Lorblanchet et Peyron de la Faculté des Lettres de Montpellier. Enfin, des photos en diapo couleur ont été faites par mes soins.

Mais revenons au mobilier lui-même. Tous les objets le omposant peuvent être divisés en trois catégories distinctes :

- objets usagés ou passés de mode, récupérés pour la refonte,
- objets neufs, mais mal venus au coulage et mis au rebus pour être refondus également.
- enfin, objets neufs ou en cours de fabrication et prêts à être livrés à la clientèle.

Mais comment expliquer la présence d'un tel ammoncellement en mer, à 500 m. de la côte et par 7 m. de fond ?

Cette question s'est posée dès que l'importance de la découverte, par son volume, fût apparente. Deux possibilités ont été retenues : cachette de fondeur ou épave.

Les dépôtsde fondeur, contenant des objets sensiblement identiques à ceux de ROCHELONGUES, sont abondants dans notre région. Ils sont attribués à la période Launacienne (de Launac près de Montpellier (34) qui fût l'un des premiers et des plus importants, découvert).

Cette explication pourrait paraître valable si la découverte avait été faite tout près d'une côte rocheuse, au pied d'une falaise qui aurait pû s'abimer dans la mer entrainant avec elle les objets qui auraient pû y être dissimulés.

Pour ROCHELONGUES, cette hypothèse n'est pas valable. En effet, le gisement se trouve à 500 m. du rivage actuel, le long d'une côte plate et stable. Il faudrait donc admettre soit un affaissement du sol, soit une montée du niveau des eaux ou bien

les deux phénomènes conjugués, le tout portant sur une variation de plus de 10 m.; car le dépôt, si dépôt il y avait, aurait dû être constitué à quelques mètres au-dessus du niveau atteint par les tempêtes les plus violentes.

Or, de plusieurs études sérieuses, en particulier celle de Monsieur Denizot, il ressort que la côte actuelle du Languedoc n'a guère variée depuis le néolithique, et que nos lointains ancêtres ont connu la mer au niveau où nous l'a voyons actuellement.

Reste donc l'hypothèse du naufrage. Quoique qu'aucun fragment de bois, aucune pièce de grément aucun reste de vaisselle n'est été découvert, elle reste la seule valable. Le bois se conserve très mal dans l'eau de mer à si faible profondeur, les tarets l'attaque rapidement, les tempêtes le disperse. Sur des épaves beaucoup plus récentes, d'époque grecque ou romaine, il est très rare que nous rencontrions des restes du navire, et quand cela s'est produit, comme pour l'Epave D d'Agde, nous n'en avons découvert que sous un ammoncellement important d'amphores, coincé dans des failles de roches.

Il en est de même pour les pièces de gréement toutes en bois vraisemblablement étant donné la rareté du métal à cette lointaine époque.

Pour la même raison, la coque devait être entièrement chevillée de bois, donc absence de clous, abondants sur d'autres gisements après la disparition du bois.

Le manque de fragments de vaisselle s'explique aussi. La poterie indigène, mal cuite n'a pû se conserver. Dans les gisements terrestres de même période, lorsque le sol est humide, on éprouve d'énormes difficultés à dégager les poteries, et ces dernières s'effritent parfois rapidement sitôt à air libre. Un séjour prolongé dans l'eau les a forcément détruites.

Cependant, le chargement est là et abondant. Il n'a pu y venir qu'à bord d'un navire qui, au 1er Age du Fer, à une période difficile à déterminer avec précisions, mais probablement vers le VIe siècle AV. J.C., si l'on tient compte des formes les plus récentes, suivait nos côtes.

Ce navire appartenant ou armé par un fondeur-récupérateur faisait du cabotage, s'arrêtant sur la grève ou pénétrant dans les fleuves cotiers pour commercer avec les populations locales, échangeant des objets neufs contre d'autres usés ou passé de mode et ce qui n'est pas impossible, pouvant fabriquer à façon et à la demande pour certains clients attachés aux formes ancestrales.

D'où venait-il ? Où allait-il ? Deux questions parmi tant d'autres que pose ce gisement et qui restent encore à résoudre. Mais qu'un jour ou l'autre, je l'espère, nous arriverons à tirer au clair.

3-th Plenary Meeting of Committee for Conservation ICOM
Madrid 2 - 7 October 1972.

J. Lehmann
Poland.

The conservation of water logged wood objects brought out from Lac of Lednica and Gdańsk Gulf in Poland.

Introduction

The Conservation Laboratory of National Museum in Poznań has performed two interesting works in water-logged wood conservation. The first executed between 1959 - 1962 was a boat 12 m long, made of one oak stem. It has been brought out during the under water archeological examination in the Lac of Lednica known as an important historical place. The King´s Castle was destroyed in the year 1038 in the battle between Czechs and Polish troops. This object important in our history had to be saved.
The second one was a number of small wooden objects from the ship " Solen" sunk during the battle near Oliwa, between Polish and Swedish war ships in 1627. The conservation of those objects has been made in recent two years. It is intended as an experiment before the conservation of bigger pieces.

1. Deterioration of the wood.

We have had two kinds of wood, scil. oak and pine in very bad condition. The shrinkage of wood is presented on the table 1.

Table 1.

Shrinkage of wood before treatment.

Sample - wood	Average shrinkage in %			
	t.	r.	l.	v.
Oak fresh	8	4	0,4	12
Oak from Lednica	26	20	1,2	54
" " Gdańsk	24	18	1,1	50
Pine fresh	9	5	0,5	14
Pine from Lednica	32	23	1,4	80
Pine from Gdańsk	30	25	1,3	75

Both the kinds of samples from Lednica and from Gdańsk , of oak and pine wood shown similar shrinkage.

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The same it is to see according to the chemical composition of wood. The wooden objects have been submerged for a long period of time. It has been done a degradation of the cellulosic components of the cell walls. This degradation has reached an advanced state, the wood has become soft like soap and has had a very low mechanical strenght. By the normal process of evaporation has ~~x~~ caused the wood to collapse. This is shown on the Fig. 1, Fig. 2 and Fig. 3. It is same oak, pine and alder wood. The chemical composition is presented on the Table N^o 2.

Table N° 2.

Chemical composition of wood before treatment /in %/

Sample - wood	Cellulose	Lignin	Hemicellulose	Ash
Oak fresh	43,6	23,8	22,8	0,3
Oak from Lednica	37,3	38,7	17,0	3,0
Oak from Gdańsk	39,2	35,8	15,9	2,7
Pine fresh	61,6	26,9	10,7	0,2
Pine from Lednica	35,7	41,2	6,1	1,8
Pine from Gdańsk	32,3	40,1	7,2	3,4

The problem of conservation such water-damaged wood involves two factors - first the removal of the large excess of water without causing of collapse and then the confering of dimensional stability on the dried wood - second the strenghening of weak structure of wood. A better designation for such state of wooden antiquities would be " once wooden objects ".

2. Treatment.

For the treatment of the boat from Lednica we have employed the impregnation with molten alum. The impregnation has been made by steam heating to the temperature of 90 ° C. when potash-alum is dissolved in his own crystallisation-water. The heating has been made 20 times every day 7 hours, till the penetration of alum was complete. The boat is now exposed in our Military-Historical Department. The dimensional stabilisation and anti-collapse prevention have been attained excellently. But it is not successful in strenghtening of weak structure of cell-walls. The wood has been staying brittle. Besides brittleness the surface of wood has been covered

Temporarly with white powder of the product of wethering of alum. We have be forced to complete the treatment on the way of repeated impregnations with 2 % solution of linsed oil and colophony resin in petrol.

More recently we have used new synthetic materials. Firstly PEG 4000 /Carbowax Shell/. It was successful as dimensional stabiliser, but not satisfactory sa consolidant. We have retained PEG as main material in conservation of lether, textiles, cords. The fig. 4,5,6, show the fragments of lether, textiles, bones from ship "Solen" conservated with Carbowax 4000.

For the treatment of big-dimensional water logged wooden objects we have elaborated a new procedure with using of urea-formaldehyde resin of Polish production /trade name Karbadur, by Chemical Factory in Pustków/. This resin is commonly used as glue in furniture production.

We have used this as 5% solution in mixture of water, ethyl-alcohol and gycerin 5 : 2 : 1 for impregnation by brushing. For impregnation by immersion we have used the same solution, but x thiner - 2%. The most important in this procedure is the addition of glycerin to the solution. It facilitate the penetration of resin into the wood and keeps the object wet. After impregnation the object is dried very slowly under the polyester foil 5-10 microns.

The catalyst of polimerisation /amonium chloride -NH_4Cl/ is added firstly after 3th or 4-th impregnation by brushing, or after a half of period of soaking by immersion. The number of brushing depends of state of wood and of thickness. We have made the brushing 6 times every 5 days, and immersion 30 days. The drying has been made 60 days under covering with plastic foil.

3. Results.

The mechanical resistance of wood after treatment has been quite excellent. The shrinkage has been reduced by about 40%. It is shown on the Table N° 3

Table N° 3

Shrinkage of wood impregnated - Lednica with alum, Gdańsk with 5% solution of urea-formalehyde resin.

8

Sample - wood	Average shrinkage %			
	tg	r	lg	v
Oak fresh	7,3	3,1	0,3	8,5
Oak f. Lednica	16,9	15,0	0,7	26
Oak f. Gdańsk	17,1	12,3	0,7	24
Pine fresh	8,0	4,5	0,4	10,5
Pine f. Lednica	17,5	12,0	0,5	28
Pine f. Gdańsk	18,0	15,1	0,7	32

The changes of volumetric weight are shown on the Table N° 4.

Table N° 4.

Changes of volumetric weight.

Sample - wood	Average weight g/cm^3	
	wood untreated	wood treated
Oak fresh	0,75	0,85
Oak f. Lednica	0,53	0,77
Oak f. Gdańsk	0,44	0,76
Pine fresh	0,54	0,59
Pine f. Lednica	0,31	0,53
Pine f. Gdańsk	0,25	0,41

The objects have been cleaned before the treatment mechanically to the original surface, and after the treatment only rinsed with cold water.

The treatment has resulted very less amount deformation of the objects. The shrinkage have been reduced to ± 40%.

The procedure of aplication is simple to carry out and involve the minimum expenditure of labour, material and equipment. The urea-aldehyde resin is used commonly in the furniture industry any tenth years ago. It seems be stable in the room conditions to ageing and not react with the material itself.

The appearance of the treated objects is very good and shows no substantially alteration.

J. Lehmann
Muzeum Narodowe
Poznań, Poland.

c/5

ICOM - COMMITTEE ON CONSERVATION

MADRID MEETING

OCTOBER 2-7, I972

CONSERVATION OF A ONE-LOG BOAT

BY

MIHAILOV A.

8981/90

NATIONAL INSTITUTE FOR CULTURAL PROPERTY

Boul. Dondoukov 44

CONSERVATION OF A ONE-LOG BOAT

Anton Dimov Mihailov - National Institute of Monuments of
Culture - Sofia

A. CONDITION OF THE BOAT

During dredging of the Varna Lake in 1970 for building the Varna-West port, a one-long boat (Fig. 1) was discovered near the Topolite Junction, 15 m from the coast at a depth of 2 metres, which lied in a layer of reeds and turf for many centuries.

The boat is 3150 mm long and 525 mm wide in its middle part where it was about 350 mm high (Fig. 2). The volume of the boat was about 0.60 m^3 and the volume of the timber about 0.32 m^3. It was covered with sea shells, roots penetrating in depth, slime, etc.

After the boat was cleaned, traces were detected indicating the manner of its carving, combined with burning which helped in treatment of the timber before its softening. This was required because of the primitive tools. Carving was done by cross cutting of veins and separating strips 40-50 mm wide and 150-200 mm long (3).

For greater stability during carving two supporting sections (ribs) were cut diving the boat in three parts, the middle one being the largest. Probably this vessel was with one seat (3). The whole front part and about a quarter of the portside board were broekn when the boat was removed and part of the timber was missing. In addition, the same board was split at the level of the bottom on the boat at a length of 1100 mm by displacement outward and upward by about 20 mm. The remainder of the front dividing section (between the fore and middle part of the boat) had a crack about 70 mm long. The hind section was broken and cracked and part of its volume was also missing. In the upper side of the section there was an artificial orifice leading to the hind part of the left (portside) board.

The starboard was [illegible] along the mid

[illegible] and was bent inwards with an arrow of the curve of 65 mm. From it a layer thick up to 25 mm and more was missing. 250 mm from the hind side of the starboard there was a mechanical damage. In the middle of the boat there was an arrow of bending (from the upper line of the missing timber) about 85 mm.

The boat timber was entirely attacked by microorganisms. It was soft altogether.

The colour of the boat after cleaning was dark brown.

Microscopically the type of wood from which the boat was made was determined, i.e. Quercus frainetto ten. In addition, the boat was made from a whole stem of tthe tree with a diameter exceeding 900 mm (Fig. 3), and the white part of the timber, with the exception of the middle part of the starboard, was not included in its volume. The main reason for the defects established before the conservation (except those from the mechanical damage during its removal), such as cracks and certain deformations, is the core, a few cm from the upper surface which runs along the whole length of the boat (in the parts which have not been carved). This core is also a factor contributing to supplementary defects in the process of conservation.

By weighing the moisture in the timber of the boat was established. It varied between 135 and 142%. Assuming that the absolute maximum moisture of the tree is 72%, this double admissible moisture is another indication for the greater destruction of the timber of the boat which reaches up to 50% and has been observed under microscope.

The mussels and sea snails stuck on the boat and found in its vicinity have been studied by workers of the Research Institute of Oceanography and Fishing in Varna. Seven types of mussels and snails [illegible] of which 3 have been accomodated to living in lake water,

since the end of the Quaternary the lakes near Varna have been a sea gulf which has been probably completely cut from the sea in the Bronze Age as all materials from the lake dwellings have sea fauna stuck on them (3).

Proceeding from the remnants of marine fauna found on the boat and near it and the great resemblance with the parts of a wooden one-log boat at the lake dwelling near Ezerovo village (similar to the one in our case) we can claim that this is the case of aboat made and used in the Bronze Age (3).

B. THEORY OF CONSERVATION

The conservation of timber which has lied for centurues under conditions of subterranean abd other waters is a difficult problem, concerning specialists from many countries. The techniques employed in the conservation of such wood with the desire to preserve its volume are various and results are from satisfactory to very good.

The progressive degradation of the chemical composition of timber, according to Mullethaller, is mainly due to the effect of microorganisms, temperature and the humidity of the environment, the aerobic or anaerobic conditions, the pH of the soil and the chemical decomposition.

The stabibity of the timber components and their resistance to microorganisms varies, part of the semi-cellulose components decaying first, followed by the celluloss and the more stabile part of the semi-cellulose components and the most stable chemical component, the lignine remain last (11).

According Mullerthaller the problem of stabilising wet timber includes two stages:

a) removal of [illegible] water without visible changes in size;

Many techniques for the stabilisation of wet wood are known such as: alum treatment; subsequent treatment with alcohol, ether and resin; burial in earth; glycerine treatment; PEG treatment, etc. (1,2,3,10,11,12).

As the boat has been submerged in water for centuries, degradation was in an advanced stage and the timber was very soft, with low physical and mechanical indicators. The weakened state of the cell wall structure would result in the ordinary process of drying in great deformations.

The drying of the Quergus frainetto ten type of oak in per centage according to B. Poikovski (Yugoslavia) is as follows: longitudinal $\alpha_l = 0.4$; radially $\alpha_r = 5.9$; tangentially $\alpha_t = 8.9$, and by vlume $\alpha_v = 16.2$. This means that after conservation the boat would reduce its length by 12 mm, its width by about 65 mm and height by about 40 mm. Any change of size results in deformations and fissures. For this reason it was necesary to make conservation very throroughly.

In our practice we have tried many techniques and ultimately we adopted as most suitable the method of Centerval and Rolph (9). Naturally in the application of this method we made a number of modifications and additions which would, according to us, inporve the final results.

In the past seven years PEG has been used in this country to conserve nose ornaments sitting long on the sea bed, a gate from the Cherven madan fortress (Samokov) from the town of Rila, cork Roman sandals and a toilet chest, part of a mast, etc. (5,6,7,8). This experience helped us to find our bearing more quickly and accurately in respect of the conservation techniques for the boat.

In drafting the final conservation regime for the boat, apart from the achievements in this field by many specialists, laboratory [illegible] dendrological investigations as well as the structure of the [illegible]

[illegible] the [illegible] of diffusion penetration in liquids were also taken into consideration.

The volume weight of the Q.frainetto ton type of oak is r_0 = 0.[illegible] g/sq.cm (5) and with the maximum possible moisture of [illegible] it is 1.24 g/sq.cm., the volume of pores "c" is about 17%, and the volume of cell walls "m" is about 43%. The size of intermycellar space is from 10 to 100 Å (12).

Water and mineral salts were conducted (which is of significance for the impregnation of timber) in oaks not only through the vessels but also through tracheids with diamter exceeding 12 μ. As the Q.frainetto ton type of oak grows in very dry and very compact soils in the summer, its vessels are much shorter as compared with those in other types of oaktrees, and the tracheid diameter is from 16.4 to 17.8 μ. The water conducting tracheas have apertures from 0.2 to 0.5 mm and are long 100 mm and even more (4).

A. Stam (USA) has established that the relation between the mollecule diffusion coefficient of a given substance in a free solution (Do) and the diffusion coefficient of the same substance in freshly cut coniferous timber is as follows: In direction along the veins D_{long} = 0.649Do, and in direction across the veins, D_{lat} = 0.045Do, or

$$\frac{D_{long}}{D_{lat}} = \frac{0.649Do}{0.045Do} = 14.4$$

If we assume that in the Q.frainetto ton timber the lateral penetration of the fibres is even smaller than the above, then the duration of the period of conservation of the boat for penetration in that direction and clarified by the technological tests is quite sufficient.

The method of conservation selected by immersion, described

[illegible]

[illegible] lower concentrations than 10% are used at the beginni [illegible] view to the more correct course of diffusion and prevention of blocking the capillaries and microcapillaries by PEG in the initial period of penetration; From 10% upwards, the concentration is increased every 5% and not every 10% so that the diffusion can take a smoother course without great pushes; the highest concentration is 90% and not 100%, and conservation ends at 80% and temperature of 65°C and not from 70 to 90°C with a view to avoiding to reach near the absolute dry state of the boat, and somewhere around 16% of moisture (water content) close to the balanced mean water content of this area (W_p = 15 to 16%); the water content of the timb is watched; the regime is clarified by stabilising splinters on separate baths; at the initial period, with a view to better penetration in depth, PEG 3000 was used, and then PEG 4000 was added, which had a favourable effect on conservation.

C. LABORATORY AND TECHNOLOGICAL TESTS

Before beginning conservation, it was necessary that a number of laboratory and technological tests should be conducted with the boat with a view to elucidating many questions required for making a high quality conservation.

1. Microbiological Investigations

The following results were obtained in the biological investigation of a piece of the boat by Senior Sceintific Researcher Svetoslav Todorov (Research Institute of Radiology and Radiation Hygiene):

a) two species of microorganisms of rod-like forms were isolated;

b) No moulds and fungi were isolated;

c) the microorganisms isolated were about 2.4 x 10.6 per gram.

2. Microscope Determination of the Type of Wood

[illegible] V. [illegible] Lisher ([illegible] of Forestry)determined the [illegible] of Q. [illegible] (Fig. 3). The wood is circle-porous. The large vessels of the spring wood are elliptically rounded forming a complete belt. The vessels of the summer wood are fine, and the lumens of most of the vessels are filled in by tilli. The small vessels of the summer wood mass form a picture in the shape of flames. The wood parenchyma is of diffusion metatracheal type. The core rays are unilinear and multiple. Very wide rays rarely occur. The annual rings are quite narrow.

3. Determining the age of the boat

For the C_{14} age determination of the boat,by a piece from it was sent to A.E. Werner, head of the Research Laboratory of the British Museum which, thanks to his kindness, is now being investigated.

4. Investigation of the strength qualities of the wood

To establish the strength radially of the non-stabilised wood fibres, a piece of the best preserved part of the boat with water content of 60% was tested for hardness in accordance with the most suitable method of Brinell tests with ball diameter of 10 mm.

From 15 tests an average result of 145 kg/cm^2 was obtained. In comparing this result with the Brinell hardness test of fibres crosswise for sound oaktree wood in 15% water content, i.e. about 450 kg/cm^2, one can see that prior to conservation the boat had 3.1 times less harness.

Also to compare it after the completion of the entire conservation process, a piece of the boat was subjected to the Brinell hardness test and a result of 450 kg/cm^2 was obtained. As is observed, this result is identical with the indicator of the hardness for the sound wood. This means that the conservation of the boat in respect of its physical and mechanical properties has been done

5. Irradiation [illegible]

Senior Researcher [illegible] and the Senior Researcher [illegible] of the [illegible] Institute of Radiology and [illegible] investigated [illegible] the opportunities of treatment of [illegible] of the [illegible] After irradiation with [illegible] ([illegible]), no organisms were isolated in the sample after 48-hour cultivation at 37°C and until the 6th day in room temperature.

This investigation was conducted with a view to a possible irradiation treatment of future finds of similar type but of smaller dimensions.

6. Laboratory Stabilisation Probes

The stabilisation probes on pieces of the boat were conducted as follows:

a) Repeated coating of a piece by Carbowax solutions (PEG4000 $HO.CH_2-(CH_2.O.CH_2)n + 1 - CH_2.CH$) with concentrations of 5, 10, 15, 20, 25 and finally 3 per cent. Gradually with the increase of the concentration of the solutions, ethyl alcohol was added to the water to assist drying from 1:1 to 1:2 weight parts.

b) Submerging a piece in PEG4000 water solution by ascending concentration from 10 to 100% in terms of 10%, at temperatures ranging from 30 to 70° (9).

c) Submerging a piece in PEG4000 water solution by ascending concentration from 5 to 90% in terms of 5%, at temperatures from 15 to 70°C.

d) Submerging a piece in PEG4000 water solution with ascending concentration from 7 to 8, 9 and 10%, at temperatures ranging from 15 to 25°C, followed by from 10 to 90% in terms of 5% at temperatures from 30 to 70°C, Finally the concentration was reduced to 85 and [illegible] at temperatures [illegible] and 65°C respectively.

e) The same variation was repeated and for concentrations up [illegible]

As these laboratory [illegible] were made on samples of [illegible] (about 30 to 45 cm³), the process of conservation was [illegible] accelerated with a view to establishing the approximately most suitable regime by concentrations and temperatures but not in time. The worst result was obtained in coating by changing PEG concentrations. Then the results were improving by the order described in paras. b, c and d, and the best stabilised probe was that described in the manner in para d.

7. Technological Stabilisation Probes

a) A piece with volume 500 cm^3, weighing 700 g and 292 mm long and about 40 mm thick was treated in the regime described in 6d. The process was terminated in water content about 18% and weight of 490 g. and the quality of PEG absorbed was 140 g., or about 40% of the ultimate weight of the wood, and about 20% of the initial. This dose was accepted as a standard both in the subsequent technological tests and in the boat's conservation. The regime continued for 65 days, or the penetration was expressed by 2.2 in length and 0.6 mm by width per day - delayed regime.

b) A piece weighing 1640 g, 800 mm long, and a piece 4600 g, 605 mm long were treated in the same manner. The different length and thickness of the pieces, as indicated above, allowed us to check here also the continuation (duration) of the diffusion longitudinally to the wood fibres. The first piece was conserved for 60 days, and the second for 80 days, with the same percentage of absorbed PEG amount, or longitudinal penetration at 5 mm per day - accelerated regime.

For the boat's conservation we adopted a comparatively delayed regime - about 2.5 mm per day. As it in its thickest part is about [illegible] mm, it should be stabilised in 450 days. To make equal the penetration of PEG and the terminal water content in the whole cross-section of the boat, the regime was extended by 25 days (Table 1

[illegible] through [illegible]

[illegible] which clearly showed [illegible] filled in by the origin[illegible]

[illegible]

8. Technological [illegible]

Three pieces of the belt were cleaned with alcohol, heating with ICL, heating with warm air, contact heating, etc. The best result was obtained in contact heating and that with hot air, followed immediately by that with pads soaked in ethyl alcohol and washed by rubbing in with a brush. At the beginning 50% ethyl alcohol was used, and later 96%.

9. Technological Tests for Protecting Treatment

The smallest piece (see point 7) was coated twice with the following composition: Paraloid - 72 weight parts, PEC4000 - 2 weight parts, turpentine 73 volume parts and toluene 21 volume parts. After ample coating, it was drived by ICL;

b) the long piece was treated in the same way in zones of 100 mm length with the following compositions: 1.Paraloid B72 - 3 weight parts, Cosmolloyd - 4 weight parts, Toluene - 93 volume parts; 2.Paralloyd B72 - 4 weight parts, Cosmolloyd - 3 weight parts and Toluene - 93 volume parts; 3. Paraloid B72 - 5 weight parts, Cosmolloyd 2 weight parts and Toluene 93 volume parts; 4. Paraloid B72 - 5 weight parts, Cosmolloyd 3 weight parts and Toluene - 92 volume parts.

Dilution was done on a water bath and the composition was applied hot.

From the above five compositions (according to "a" and "b"), the best results were obtained with the last two.

c) [illegible] one of its halves by th[illegible] [illegible] parts, naphtha oil [illegible], [illegible] volume parts, [illegible]ethaniol [illegible] and the [illegible]

[illegible] composition but the copper naphthenate [illegible] re- [illegible] by Cobalt naphthenate.

After ample repeated application with these two compositions heated to about 80°C and drying, additional application with the above-mentioned composition [illegible] made. Of the two hydrophobe compositions that with copper naphthenate proved to be better because apart from its property (as well as of the cobalt naphthenate) to assist the saturation of the double links of the linseed oil, i.e. its drying. it also has good antiseptic and hydrophobic properties.

10. Conservation of the Boat.

Before beginning the conservation of the boat, it was cleaned with a soft water stream, with vortreiber and root scalpels, seaweeds, sea shells, etc. (Fig. 6). Greasy stains were formed during the cleaning of the boat and they practically disappeared on the second day.

Before the boat was placed in the bath, the latter was filled with 7-% PEG3000 solution at one-third of its height. After the boat was placed on the supports, aditional solution was added to cover it by a layer of 50 mm. The concentration and the temperature of the solution were maintained strictly in accordance with the regime given in Table 1 and Fig. 5. It was warmed by the combination of four electric heaters of varying capacities. The solution was agitated to avoid its sedimentation. In the same way, suitable temperature preventing considerable coolings was also mainted in the room where the bath was placed.

The humidity of the wood was determined by the weight method [illegible] previously weighed samples.

After the conservation, the initial weight of the boat, [illegible] of the [illegible] weights of the [illegible] and wood [illegible]. As it is impossible to fill in all pores and

[illegible] volume [illegible] from [illegible] to [illegible], [illegible] during part of the conservation process has [illegible] not [illegible] [illegible].

The conservation process was [illegible] by the regime until the indicated water content (humidity) of the respective control sample was obtained. Irrespective of the fact that between the boat humidity and the sample there was often significant difference, after the defined parameters of the solution were maintained for a given period, the wood of the boat approached this humidity (water content). With this particular purpose and because of the danger of deformation in case of a drop of humidity under 32% (the point of fibre saturation being 22%), the regime over 65% concentration and under 58°C until humidity of 16% was reached was extended for each individual stage. After the stabilisation of the respective humidity (water content) and termination of the absorption of PEG, the next parameter of the regime was begun.

Glycerine was added to PEG solutions containing concerntrations higher that 40%, i.e. 0.5% in 40%, 0.5% in 60%, 1.5% in 80% and 0.5% in 90%. The glycerine added was used as plastifier, namely yo prevent the filing of PEG on the wood surface on one side by forming a mollecular layer around the macromolleculos, which on the other hand increases the distance between the separate macromolleculos making them mobile and in this way facilitating their penetration to a greater depth.

To prevent the transformation of the insoluble sodium pentachlorphenol in water into an insoluble pentachlorphenol, an eye was kept on acidity which should not exceed 7.5 to 10 (9). In our case it ranged from 7.5 to 8 for which reason there was not need for [illegible] by the addition of sodium carbonate.

As is seen on Table 1, the maximum concentration of the solu-

[illegible] in the previous [illegible] view to achieve equal [illegible] of PEG along the [illegible] cross section of the boat, we used [illegible] conditions of the impregnating parameters maintained for a total of 70 days.

Gradual cooling of the solution to 55°C was made after 475 days, after which the boat was removed by a special lifting device (Fig. 7). The room was warmed to 40°C and the temperature was reduced to 32 - 34°C in the course of 5 or 6 days.

Cleaning of the boat surface from PEG was done in accordance with the technological tests, i.e. by warming and wasjing of the molten mass by vertreiber and pads soaked in ethyl alcohol at the begining 50% and at the end 96% solution (Fig.8).

After the boat was cleaned, the last concluding protective treatment by double application with composition 4, given in Section C§b, was made.

CONCLUSION

The adopted method of conservation of the boat proved suitable. It was conserved very well with insignificant increases of the preliminary deformations and cracks. The outside appearance was good and the colour preserved. (Fig. 10 ~~& 11~~). After the protective treatment the boat was exhibition under ordinary conditions in the first hall of the Archaeological Museum near Varna (Fig. 11).

Analysing the conservation process (Table 1) and the respective results, it should be emphasised that the duration in time of the conservation regime of an object similar in type and conditions, without deteriorating its quality, can be reduced under 400 days. This can be easily seen on Fig. 5, on the basis of which a respective [illegible] graph [illegible] drafted for each individual case.

R E G I M E [illegible]

[illegible]

[illegible] tion concen- tration in %	t°C	Rela- tive weight of so- lution at 30°C in g/cm³	[illegible] humidity of wood in %	Length of [illegible] period in days	NOTES
7	15	1.013	140	5	Zone above point of saturation of [illegible] accel. regime with exception for humidities from 32 to 24%
8	17.5	1.014	133	5	
9	20	1.016	126	4	
10	25	1.017	119	4	
15	30	1.025	104	14	
20	35	1.031	92	15	
25	38	1.037	82	15	
30	40	1.044	74	16	
35	42	1.052	66	16	
40	45	1.060	59	17	
45	48	1.068	52	17	
50	50	1.076	45	18	
55	52	1.084	38	18	
60	55	1.092	32	21	
65	58	1.100	28	24	
70	60	1.108	26	27	
75	62	1.116	24	30	
80	65	1.124	22	33	Zone under the point of saturation of wood. Delayed regime. Finally the process is delayed under resp. parameters for making similar PEG penetration, wood humidity in the whole section of the beam.
85	68	1.132	20	36	
90	70	1.140	18	39	
87	68	1.133	17	16	
90	70	1.135	15-16	16	
85	68	1.132	15-16	30	
80	65	1.124	16	40	

TOTAL DURATION OF THE REGIME IN DAYS: 475.

[illegible]

1. [illegible] - [illegible], Stockholm, [illegible]
2. [illegible] - [illegible], [illegible], [illegible] 1970.
3. Ivanov I. - Prehistoric Boat in the Varna Lake, communication at the Archaeological Conference, Balchik, 1971.
4. Kalinkov V., Shipchanov I. - Investigation on the structure of the wood of some of our oaks, Collection "Manufacture and Compl Use of Oak Wood". Intern. Symposium. Zemizdat, Sofia, 1970.
5. Mihailov A., Vulkova N., Zaharieva E. - Conservation of Exhibits made of Oak Wood and Removed from the Sea Botton. Collection "Manufacture and Complex Uso of Oak Wood". International Symposium. Zemizdat, Sofia, 1970.
6. Mihailov A., Zaharieva E. - Conservation of the Gate of the Cherv Fortress, ~~[illegible]~~ Muzei i Pametnitsi na Kulturata magazine, No. 2, Sofia, 1968.
7. Mihailov A., Zaharieva E. - Conservation of Madana in Rila town, Durvoobrabotvashta i Mebelna Promishlenost magazine, Nos. 5-6,197
8. Mihailov A. - Conservation of a Wooden Chest for Toiletries and of Cork Lafies' Soles of the excavations in Tulovo. Muzei i Pametnitsi na Kulturata magazine, No. 4, Sofia, 1971.
9. Moren Rolf and Centerwal Bertil - The Use of Polyglycols in the Stabilizing and Preservation of Wood, Technical Information MoDo., Stockholm, 1960.
10. Moren Rolf - Some Practical Applications of Polyethylen Glycol for the Stabilisation and Preservation of Wood, Technical Information, MoDo., Stockholm, 19[illegible].
11. Mullstaller Bruno - A paper on the research on the preservation of wet wood, Paris, [illegible] ([illegible] translation).
12. [illegible] H. - Conservation and Restoration of Antiques and Works of Art. ([illegible] English). [illegible], Sofia, [illegible].

FIGURES

Fig. 1. General appearance of the boat immediately after being taken out of lake.

Fig. 2. Plan (drawing) of the boat.

Fig. 3. Drawing of making the boat from the trunk of the oaktree.

Fig. 4. Microphotograph of a cross section of wood from the boat.

Fig. 5. Diagram of the conservation regime of the boat.

Fig. 6. Cleaning the boat from slime, seaweeds, ~~xxxx~~ etc.

Fig. 7. The lifting mchenanism.

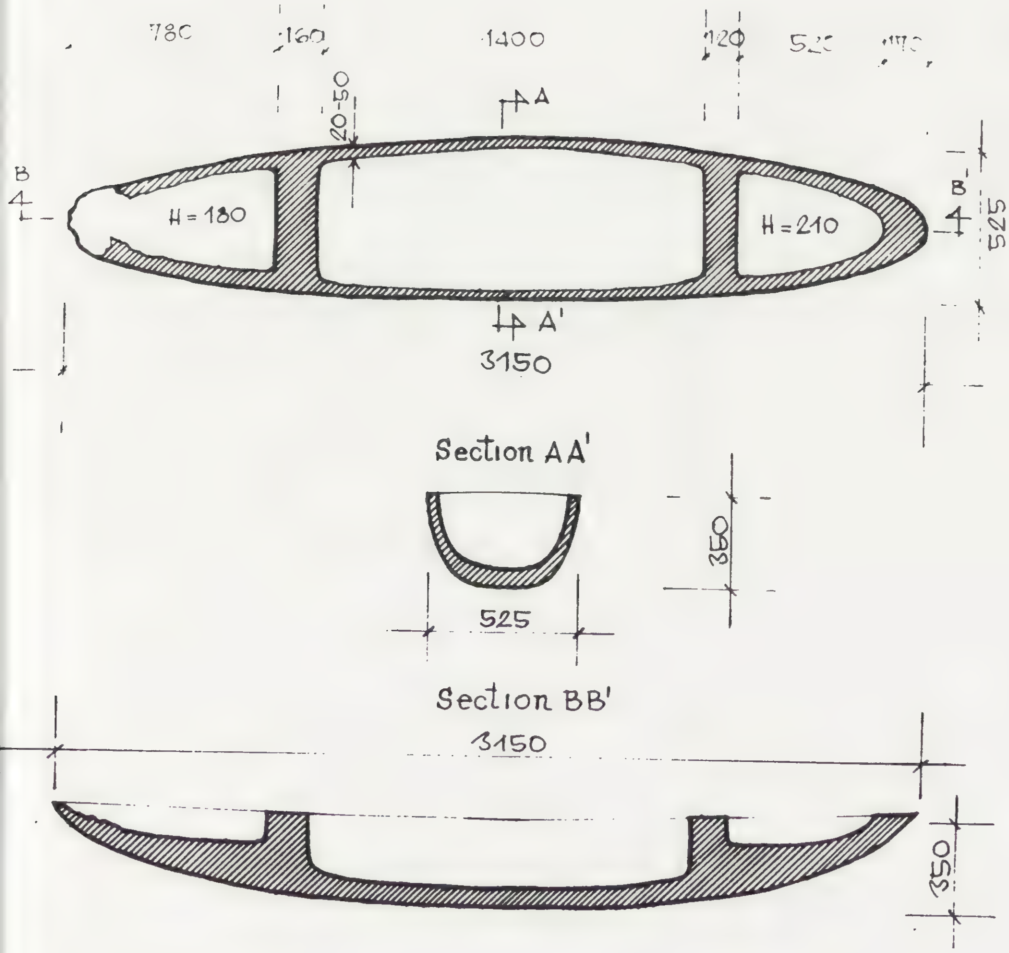
Fig. 8. Cleaning the boat from PEG.

Fig. 9. Hydrophobisation of the boat.

Figs. 10 ~~& 11~~ Appearance of the boat after conservation.

Fig. 11. Appearance of the boat after exhibiting.

Fig 1


780
160
1400
120
525
20-50
A
A'
B
B'
H = 180
H = 210
525
3150
Section AA'
350
525
Section BB'
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350

fig. 2

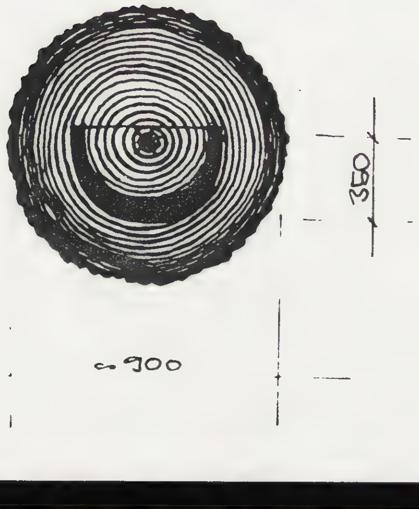
350
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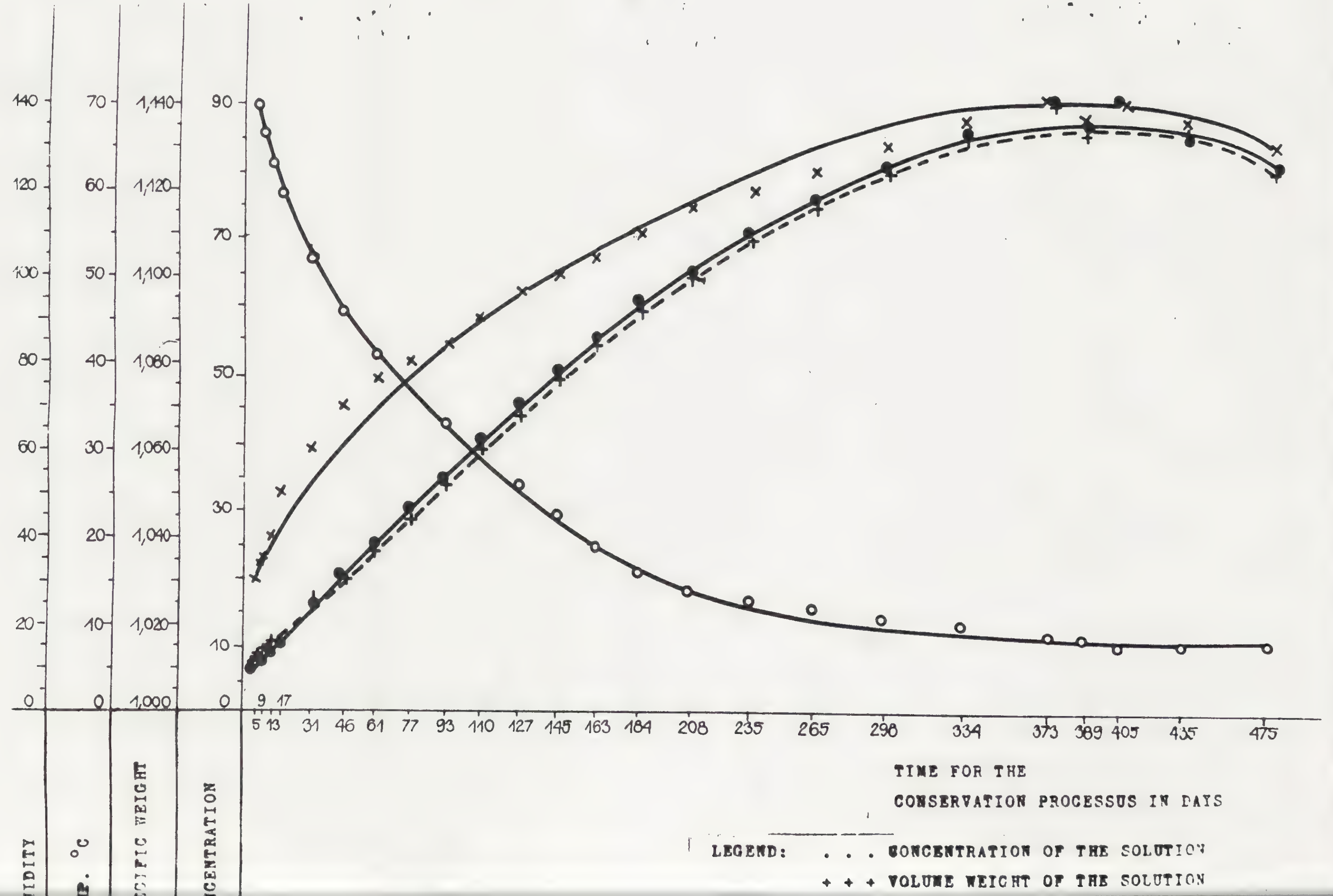
fig. 3


IDITY
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60
80
100
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140
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0
10
20
30
40
50
60
70
CIFIC WEIGHT
1,000
1,020
1,040
1,060
1,080
1,100
1,120
1,140
CENTRATION
0
10
30
50
70
90
5 9 13 17 31 46 61 77 93 110 127 145 163 184 208 235 265 298 334 373 389 405 435 475
TIME FOR THE
CONSERVATION PROCESSUS IN DAYS
LEGEND:
. . . CONCENTRATION OF THE SOLUTION
+ + + VOLUME WEIGHT OF THE SOLUTION

fig. 6

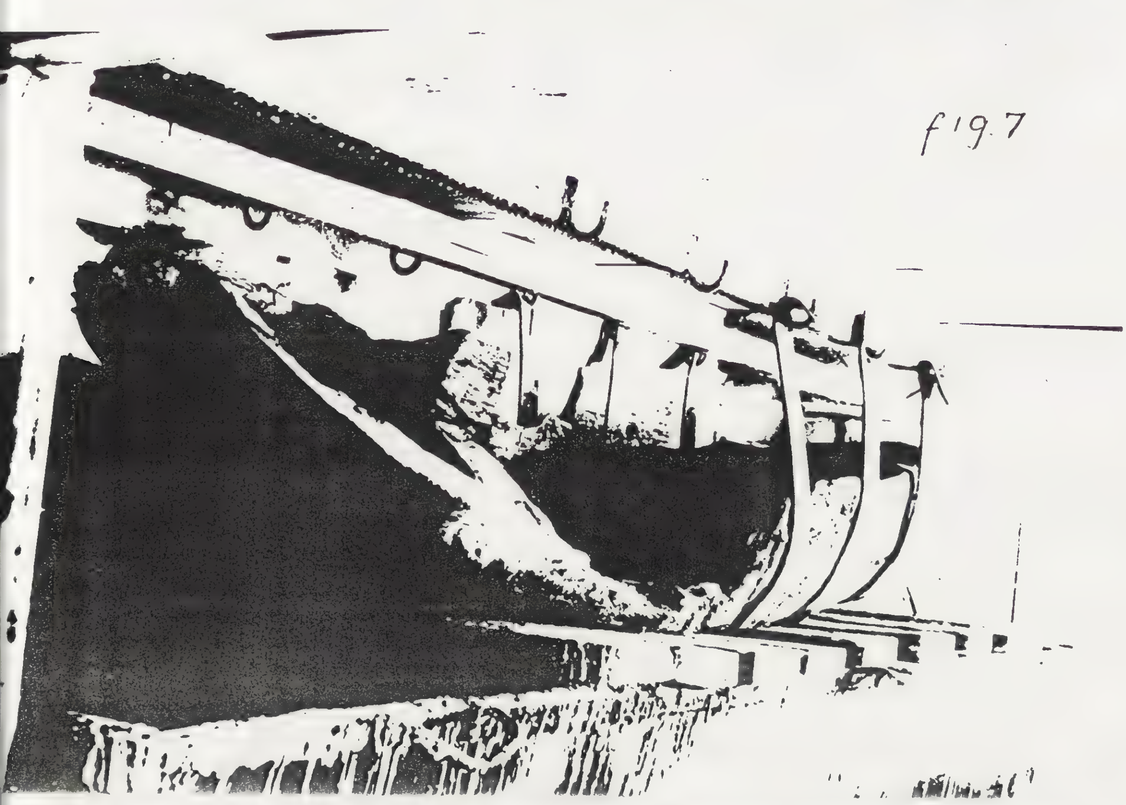

fig. 7

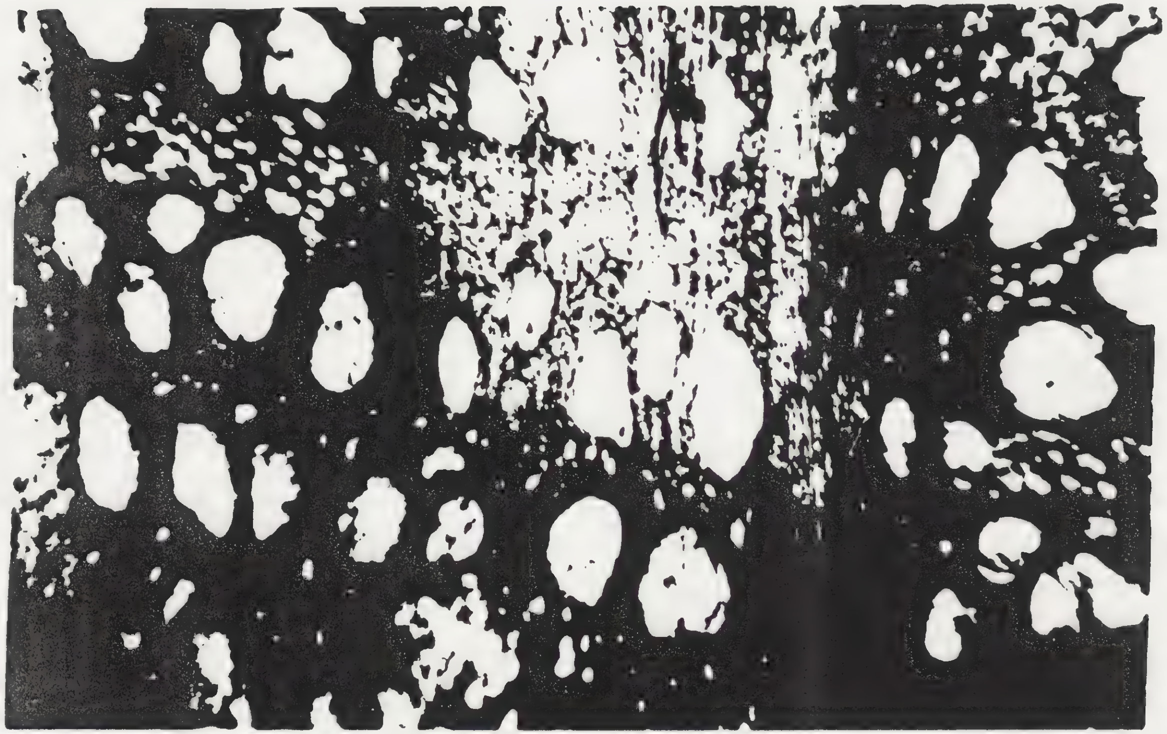

fig.4

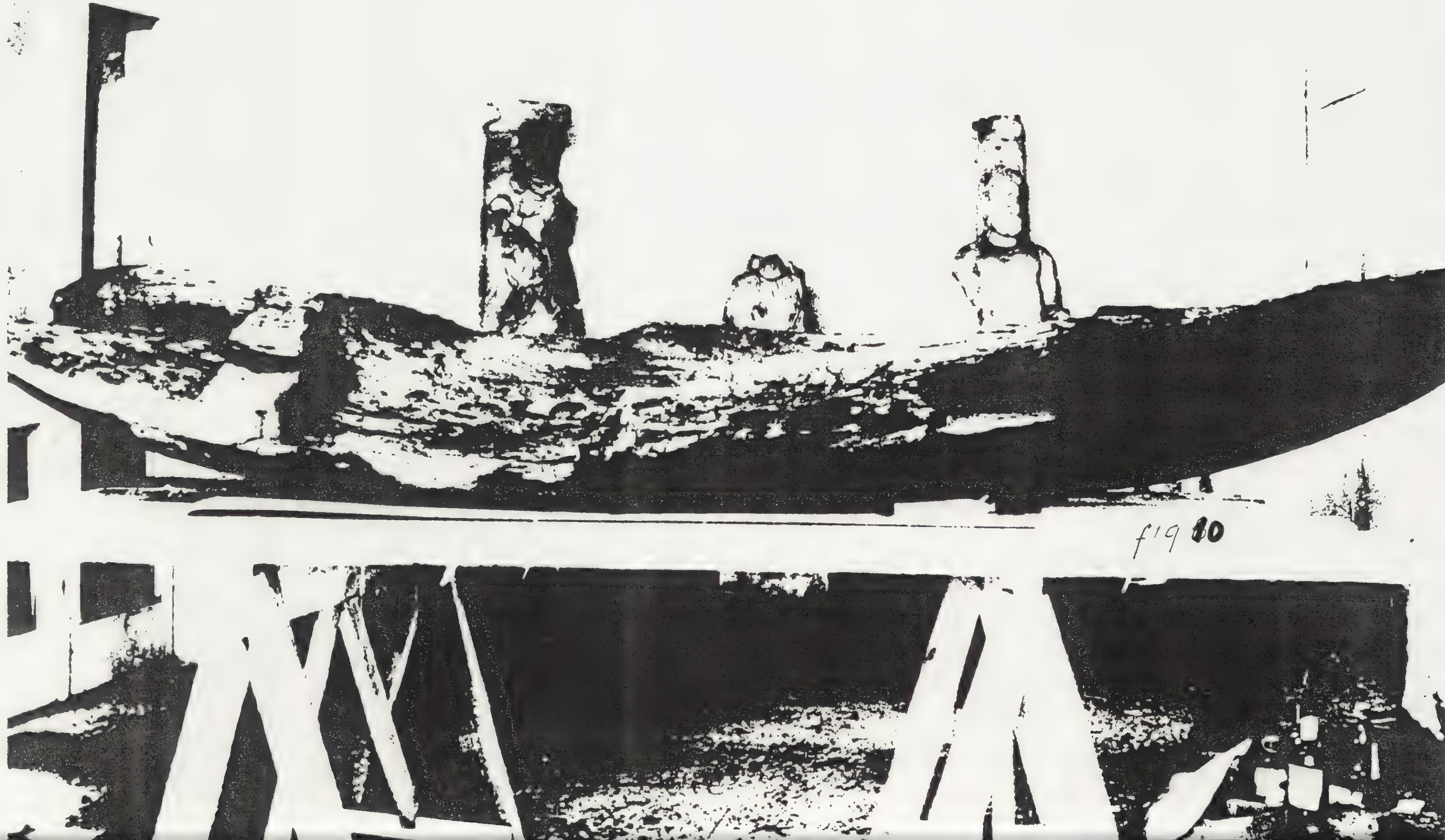

fig 10

fig. 8

fig. 9

CORRECTED

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THE INTERNATIONAL COUNCIL OF MUSEUMS
Committee for Conservation

CONSEIL INTERNATIONAL DES MUSEES
Comité pour la Conservation

Madrid: October 2 - 8
1972

THE "VIRGEN DE LAS ANGUSTIAS" (Virgin of Sorrows) BY JUAN DE JUNI

A STUDY FOR ITS PRESERVATION AND RESTORATION

Alberto Recchiuto Genovese
Spain

002180

THE "VIRGEN DE LAS ANGUSTIAS" (Virgin of Sorrow) by JUAN DE JUNI

A study for its preservation and restoration

by Alberto Recchiuto Genovese

Foreword

The "Virgen de las Angustias" is a polychromed wooden carving by Juan de Juni, belonging to the Brotherhood under the same denomination, and is placed in a Chapel of the Penitentiary Church of the Angustias, at Valladolid. It is popularly known by the name of "Virgen de los Cuchillos" (Virgin of the Knives). At the end of the year 1969, anniversary of the quarter-centenary of the Brotherhood foundation, the image of "Virgen de las Angustias" was moved to the "Museo Nacional de Escultura" at Valladolid being deposited there, while some repair works were undertaken in the Virgin's Chapel, in the Penitentiary Church under Her appellation. In the course of its transitory permanence in that Museum, the Directress checked the conservation status of the sculpture, very defficient in someways, and she consulted the "Instituto Central de Restauración de Obras de Arte", in Madrid, in order to request the nécessary advice to treat it, with a view to its preservation in the future. Having completed all legal proceedings (1), on April 16, 1970, the Virgin image arrives at the "Instituto Central de Restauración de Obras de Arte", in Madrid, from Valladolid, to be submitted to a treatment for its preservation and restoration, which was concluded in the month of February of 1971 (2). It was immediately taken back to Valladolid where it was placed, after exposing it, in its customary place.

This work, is, among the production of single figures by "Juni", one of the most important pieces and its execution may be dated in 1570, some seven years prior to the artist's decease. At the time, he was also working in the "Burial" of the Segovia Cathedral.

In this Virgin's image is materialized the "Compassio Mariae" of northern gothic backgrounds. Although almost all of representations of the Virgin made by Juni have

a dramatic touch, there are some, that depart from the line. Examples therefor are "The Purísima" made for the Funerary Chapel belonging to the Benavente family in Santa María de Rioseco (1557), of a great serenity and idealization. We may also see nearly happy expressions both in the "Virgin with Jesus Child and Saint John" (at Santa Marina, of León) or in the "Virgin with Child" belonging to the Becerril de Campos Church (at Palencia). (3)

The "Virgen de las Angustias" is a pathétic representation of the Mother of Christ collapsed at the Cross foot. This is a larger than natural size, conceived in monumental terms following the italian use. It is sovered with such expressive drapery, that they remind those made by Claus Sluter and Jacopo della Quercia, the vinculation with the latter having been noted first by Weisse, and then by Camón Aznar.

The composition in this sculpture, in closed line, shows in its attitude, besides that torsion typical of Juni's figures, the manneristical "contraposto". Solidly constructed, it all dinotes a great sturdiness.

This wonderful sculpture, in which the checked pain acquires superhuman appearance, manifests in its brow with open and gasping mouth, as well as in the hed tilting, the effect which on the artist produced the Laocoon, even the reason producing this expression comes from a different origin in both cases (4). The Virgin's expression and attitude move to tenderness and compássion (5). Her brow is still femenine, in spite of the fact that its strength and proportions always escape from weakness.

A very proper description of the "Virgin of Knives", is in my opinion, that made by Bosarte. Dielafoy also makes a description of this sculpture, as well as of the environment surrounding Her. (6)

LABORATORY TEST

The sculpture's dimensions are as follow:

Height :	1,27 mts.
Depth :	1,22 "
Width :	0,90 "

The Virgin is dressed with robe, upon robe(open in the front side) and cloak. Between the head and the cloak covering it, is placed a veil which,surrounding Her face and covering part of the chest, is caught up upon the right shoulder.

Sculpture

The block on which the sculpture was carved is built of pine wood (Pinus Pinea)(7). It is formed by a score of main trunksof some 20 cmts. diameter, flattened on their edges and laterally linked. The block is hollow, letting be seen in the inner part, the cross-section or head of the above mentioned constituting elements. Links are reinforced with vegetable fibers. The structure is completed with some wood additions to obtain a block capable of definitively configurating the sculpture volumes. Its base is almost oval. It may be seen in its perimeter fifteen unions of the wood parts. The open space on the base is crossed in the larger axis senses by a wooden beam fixed by means of two spikes placed on its ends (fig.nº 8).The sculpture base is enclosed within fourboard pieces placed transvérsally in regard with the longest axis. This base is placed forming a triangle with three metal wheels allowing to move the image. (fig. nº 9).

Preparation and Polychromy (8)

Polychromy preparation in all samples tested is a gypsum layer of approximately one milimeter of average thickness, with wide variations according with the support irregularities. In the preparation surface there is observed an impermeabilized area 40 microns thick corresponding to the impermeabilization,probably made with glue. Flesh colours "a polimento" have an oily binder.They are made in clear colours ranging between pinky white and pastel red. (9).

The mouth is of a dross red colour (10).

In the deepened areas of the face surface,less rubbed off therefore, there may be seen traces of an orange-reddish colour coating (11).

The shade of the hands, is similar to that of the face.

Flesh colour coatings, applied upon the impregnated preparation, is made with lead white,as major component and calcite.These whites are coloured with thinly divided vermilion, and may also be seen larger sized crystals. There are also sporádically some azurita crystals. In one of the analyzed samples, corresponding to flesh of one of the cheeks, it may be seen upon a varnish film a thin white layer with red crystals of similar characteristics to the above described components. The adherence of these layers, of oil colour, with the underlying coating is weakened and it is probably due to the impermeabilizing substance nature. (figs. nºs. 10 and 11). The veil surrounding the face is of a yellowish whitish colour(12). It shows no decoration,except for a slight serrate carved on its edge. Upon the original lead white coating,there are some superimposed coatings,among which are placed a thin varnish coating (figs nº 13).

The draperies are made with aquous agglutinant.

The over-robe, open in the front part, shows a coloration ranging from bright red to pastel red(13) and is decorated,entirely, with cartouche themes and volutes in a darker colour within the shade:from bright red to pink(14).Lights are heightened in white(see sketch and figure nº 18).The over-robe undercoat colour shows a coating(single or double) applied upon the impermeabilization film,constructed with lead white and vermilion crystals;upon this there is another transparent layer made with calcite crystals coloured in red with an organic lacquer, that could be maddor. Superimposed on the latter, there is a y yellowish varnish coating,with a thickness compárable to the above(50 microns) on which it may be seen a layer of dirt and dust(figs.nos. 14 and 15).The over-robe edge is filleted in its full length by a narrow band of plain gold.The over-robe foundation is a gold-varnish made with a coat of lead white mixed with calcite,with a few vermilion crystals and some animal black.Upon this coating is applied a gold film and then a brown coloured varnish(fig. nº 12).The robe of Bordeaux red colour (15) offer no decoration,and it may only be seen some parts of it,in the areas uncovered by the over-robe.

The cloak shows two shades corresponding to obverse and reverse. The former is of a grayish green colour(16), fully decorated with cartouche thimes and other Renaissance elements, having incorporated in its center human figures or simply heads. The dicoration is completed with curved and spiral lines. This decoration is of a darker colour than that of the background, within the same colour shade, with light heightened in white.
The cloak's edge has a plain gold selvage(see sketch and figure nº 19). The background colour structure corresponding to analyzed samples, comprises three layers starting from an impermeabilizing film. The deepest one is a layer composed of calcite and animal charcoal; upon it, there is a coating of lead white and calcite, and a further coating in blue colour made with "Smalt"(fig. nº 17).

The cloak's reverse side, of a grayish turquoise colour(17) is decorated with two stylized vegetable themes, alternating among them, executed in gold with the so-called "al mixtion" technique, similar to the remaining gold details in the figure(see sketch and figure nº 20). This structure colour is more simple, of some 60 microns of thickness, denoting the existence of only one colour coating composed of azurite, in its larger part, and malachite. Some isolated red vermilion crystal may be seen. (see fig. nº 16).

THE WORK PRIOR TO ITS RESTORATION

Support

The wooden structure forming the carved work let us see, as a consequence of the movement of the various parts forming it, through traces existing in the pólichrome coating, many linking lines of the wooden pieces. This, consecuently, marred the sculpture's beauty, especially those crossing the right hand and face. A good part of these lines, marking the wood joints were communicated with the inner hollow side of the figure, creating a "light" between the figure outside and inside.

In the area forming the robe's edge plaits, close to the left leg, as well as on the back side, there could be seen the presence of typical galleries and holes of eliptic section made by Cerambicide larvae denominated "Hylotrupes bajulus", whose attack was deeply intense.

The wooden pieces closing the sculpture on its base had also signs of attack from another xylophagous insect denominated "Anobium punctatum".

The polichromy

The face's colouring a llows us to see the union lines of wooden pieces,as a consequence of separation thereof with loss of the preparation coating and paint especially nóticeable those crossing the right cheek in a horizontal sense which,crossing it diagonally, passed the chin and reached to the upper part of the neck.

There could be observed polichromy losses in small areas corresponding to the right half of the face; upper part, edge and side of the nose,edge of the lips and chin.

The right hand flesh shows two kinds of alterations. The former was produced by the materials natúre, such as the cracks observed mainly that crossing transversally the right hand at the level of the knuckles; the latter are the results of mutillations due to the use at worship. The flesh of index,middle and ring fingers was badly damaged and the small finger had, also, lost all its polichromy and was fully destroyed(fig.nº 21).

Indiscriminated prior interventions

In the figure's back there was a hole,of rectangular section measuring 22 x 8 cmts. per side and 5 cmts. deep,made in order to attach a cross. Besides this intervention,which meant that it was necessary to take off part of a plait of the cloak,by the small hill forming the figure's seat,it was found in the back,at the height of its center,an iron piece forming á regular pentagon With 7 cmts. of side.When this iron fragment was raised,another piece of iron forming a "loop" measuring 9,5 x 3,5 cmts. was found; besides this, there was another box made in a similar way to that of the above hole,which it is assumed to have carried previously the same iron.This system to attach the cross(see fig. nº 22) necessitated the mutillation of two cloak areas in order to fix the flat iron piece,perforation of three large orifices with more than 2 cmts. dia-

meter passing through to the inner side,as well as other 40 smaller holes possibly made by introducing iron nails. In the robe's lower part,two holes with more than 2 cmts. diameter were made in order to fix it, to the "paso" (canopy throne).

On the chest there were seven metallic cubic pieces with some 6 mm. of side, threaded in their central part allowing support for seven silver knives which,some of them intercalating between the right hand fingers,aim to the center of the Virgin'chest.

In the head's upper part, a hole was made in order to permit setting a silver resplendence through the introduction of a shaft attached hereto.

Treatment

The preservation and restoration treatment(see fig. 23) applied to this piece in the Sculpture Department of the I.C.R. by restorers,brothers Cruz Solís,mainly consisted of the following points.

1st.- Desinsectation of the wood using paradichlorine-benzene 5%.
2nd.- Consolidation of unadjusted parts,interposing in the most pronounced openings, thin wooden wedges attached with vinyle poliacetate adhesive.
3rd.- Elimination of all attaching systems for the cross to which reference is made in the paragraph related to previous interventions;
4th.- Cleaning of surface,using solvents mainly composed on the base of butilamine and n,n'-dimethylformamide.
5th.- Some disturbing broken areas were stucco-plastered.
6th.- Stucco was coloured, matching the colour with that of adjacents areas.
7th.- Application of a final varnishing.

About the problems of the knives

The seven knives fixed to the Virgin's chest created a particular problem. It is very difficult to believe that a sculptor with such means for richness in

gramme ″NUCLEART″

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UTILISATION DU
YONNEMENT GAMMA
POUR LA CONSERVATION DES
BIENS CULTURELS

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LE BOIS

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COMMISSARIAT A L'ENERGIE ATOMIQUE
ECTION D'APPLICATION DES RADIO-ELEMENTS
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ONSEIL INTERNATIONAL DES MUSEES (ICOM)

COMMISSARIAT A L'ENERGIE ATOMIQUE
Département des Radioéléments
Section d'Application des Radioéléments

UTILISATION DU RAYONNEMENT γ POUR LA CONSERVATION DES OBJETS EN BOIS

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UTILISATION DU RAYONNEMENT γ POUR LA CONSERVATION DES OBJETS EN BOIS

L'utilisation de l'énergie nucléaire a plutôt commencé sous la forme d'un grand soleil rouge destructeur qui a quelques peu masqué les applications pacifiques de cette nouvelle forme d'énergie. Ces applications se sont fait jour dans la plupart des secteurs industriels, les principales ont porté sur la production d'électricité et sur les utilisations de radioéléments. Les radioéléments, sous entendu artificiels, crées par irradation d'éléments naturels dans des réacteurs nucléaires ont trouvé des utilisations nombreuses que l'on peut très grossièrement grouper en deux chapitres :

- Destruction biologique, par exemple : destruction ou stérilisation d'insectes, destruction de bactéries ou de virus.
- Initiateur de réactions chimiques, par exemple : polymérisation, réticulation, greffage.

Devant l'importance des débouchés possibles de ces applications, il convient de se demander quel bénéfice pourraient en tirer les biens culturels dont la conservation devient chaque jour plus préoccupante, surtout lorsqu'on les considère sous l'aspect de traitements de masse destinés à consolider, renforcer, conserver tout ce qui dans nos patrimoines, sans être des chef-d'oeuvres, constitue le fondement de notre civilisation.

Après avoir rappelé les principales propriétés des rayonnements issus des radioéléments, nous considérerons deux aspects essentiels de leur utilisation possible sur le bois : la destruction des insectes et parasites divers et la protection par imprégnation totale de monomères plastiques.

A. Les rayonnements.

Nous ne donnerons ici que les idées générales sur les rayonnements, réservant les éléments de calcul physique pour une annexe à ce texte. On a l'habitude de classer les radioéléments artificiels en émetteurs :

- de rayonnement α, constitué par l'émission de noyaux d'Hélium (deux protons et deux notrons) relativement lourds, peu pénétrants et de ce fait d'emploi très limité. C'est le cas, par exemple du Polonium 210.
- de rayonnement β , constitué par l'émission d'électrons déjà beaucoup plus légers mais toujours particulaire, de pénétration plus importante que le précédent et dont les plus connus sont le Krypton 85 gazeux et le Strontium 90. Ce type de rayonnement ne semble pouvoir être utilisé que pour la bétagraphie ou radiographie par du rayonnement β , d'objets assez minces comme des feuilles de papier ou des parchemins.
- de rayonnement γ. On est ici en présence d'une onde électromagnétique très pénétrante produite le plus généralement par le Cobalt 60, le Césium 137, l'Iridium 192, etc...

Nous ne parlerons ici que des applications de cette dernière forme de rayonnement, la plus prometteuse. On caractérise un émetteur γ par :

- Son activité, exprimée en Curies (un Curie = $3,7 . 10^{10}$ désintégrations/seconde). Cette quantité indique le nombre d'atomes qui disparaissent, par seconde, au cours de l'émission du rayonnement γ .
- Sa période : c'est le temps nécessaire pour que l'activité soit réduite de moitié. Cette durée peut être courte ou au contraire très longue, par exemple : Cobalt 60 T = 5,3 ans, Césium 137 T = 30 ans.

- Son énergie ; il s'agit de la quantité d'énergie émise au cours d'une désintégration, par exemple à chaque désintégration d'un atome de Cobalt 60, il y a émission de deux photons γ d'énergie 1,17 et 1,33 MeV (Million d'électrons-volts)(1). Cette énergie indique également la pénétration d'un rayonnement dans un matériau donné. (Voir Annexe).

Ces radioéléments sont fournis sous forme de "sources" dans des emballages doubles d'acier inoxydable, destinés à prévenir toute fuite de matière (Contamination). On trouvera dans les catalogues des divers fabricants les caractéristiques de ces "sources".

Nous avons dit que ces rayonnements étaient biologiquement nocifs et très pénétrants ; ceci sous-entend que leur emploi demande des précautions pour éviter tout risque sur le personnel. Les protections les plus employées sont le béton et l'eau avec des épaisseurs de l'ordre respectivement de 1,50 m et 4 m pour une activité de quelques 100 000 Curies de Cobalt 60. La nécessité de ces protections montre l'obligation d'utiliser des installations spécialisées pour l'emploi de ces sources de rayonnement. Le nombre de ces installations croît chaque année et, du fait de ces nouvelles possibilités, il devient important d'étudier les applications possibles de ces rayonnements aux biens culturels. Il faut encore signaler que les matériaux soumis à de tels traitements ne peuvent en aucun cas devenir eux-mêmes radioactifs : leur manipulation après irradiation est donc absolument sans danger. Seuls les flux de neutrons, thermiques ou rapides, et de photons γ de plus haute énergie (10 Mev, par exemple) peuvent produire une telle activation.

(1) 1 Mev = $1,6 \cdot 10^{-6}$ ergs = $1,6 \cdot 10^{-13}$ Joules

Avant de parler des applications, il faut définir ce que l'on appelle la dose ou quantité de rayonnement reçue par l'objet irradié, l'unité en est le Rad (un Rad = 100 ergs/g) avec comme multiples le Kilorad (10^3 Rad) et le Mégarad (10^6 Rad). On définit également la vitesse d'application ou débit de dose, exprimée en Rad/heure, Kilorad/heure, etc.

B. Destruction des Insectes et Champignons.

Nous avons dit que les rayonnements et en particulier le rayonnement γ pouvait jouer un rôle de destruction biologique. Ceci nous amène donc à la quantité d'énergie nécessaire pour tuer certains individus. Cette dose léthale est de l'ordre de quelques centaines de rads pour l'Homme, quelques dizaines de milliers pour l'insecte, quelques mégarad pour les bactéries, etc... Pour les insectes, qui nous intéressent ici, le phénomène est un peu plus complexe selon que l'on s'adresse aux oeufs, aux larves, ou aux adultes. Sans entrer dans les détails, nous dirons que pour la quasi-totalité des insectes connus, une dose de 25 000 rads suffit soit à détruire les larves, soit à empêcher l'éclosion des oeufs, soit encore à stériliser les adultes, amenant ainsi la disparition très rapide de la colonie.

Il est bien évident qu'un tel traitement n'empêche absolument pas l'objet irradié d'être envahi de nouveau dans un délai plus ou moins long, dépendant essentiellement de ses conditions de stockage. Il faut donc, lorsque l'on veut étudier l'influence du rayonnement sur les matériaux constitutifs des objets, envisager qu'ils subiront dans leur existence, un nombre important de traitements successifs.

Nous avons choisi, un peu arbitrairement, d'étudier ces modifications de structure après application de la dose équivalant à 100 traitements. D'autre part, il est extrêmement difficile, dans la pratique, d'irradier de façon absolument homogène un objet de forme

complexe. On admet assez couramment que la dose peut varier du simple au double selon l'emplacement du point de mesure. Ce qui nous conduit à utiliser comme dose d'étude la dose de :

25 000 x 2 x 100 = 5 mégarad.

On ne peut pas très facilement donner une durée de stockage possible entre deux traitements, si dans d'excellentes conditions cela peut être 10 ans, dans d'autres plus mauvaises (pays tropicaux, par exemple) la répétition doit sans doute être annuelle. Ce qui revient pour nous à démontrer que l'action des cent traitements successifs est inférieure à celle du simple vieillissement d'un siècle ou de dix siècles.

C'est dans cet état d'esprit que nous avons collaboré à des travaux effectués par le Musée des Arts et Traditions Populaires (Mr. Delcroix) qui seront publiés dans la revue de l'Ethnographie Française. Ces recherches ont montré que la dose de 5 Mégarad n'avait aucune incidence pratique sur les propriétés physiques et l'aspect des bois testés. D'autres essais ont montré que les propriétés physiques commençaient à être altérées de façon importante pour des doses de rayonnement vingt à trente fois supérieures, mais que même dans ce cas, les modifications d'aspect restaient extrêmement faibles.

La plupart des objets ne sont pas constitués uniquement de bois et si ce matériau reste le plus important, il faut également envisager l'action de cette dose de 5 Mégarad (représentant 100 traitements) aux tissus, papiers, colles, pigments, vernis, etc... C'est le but que nous poursuivrons dans les prochains mois.

En ce qui concerne la destruction des champignons et moisissures, des travaux conduits, avec notre aide, par le centre de Recherches sur la Conservation des Documents Graphiques (Mme. Flieder) et portant sur la destruction des champignons du papier, nous montrent déjà que les doses de destruction d'une colonie de moisissure peuvent être beaucoup

plus fortes que la destruction des insectes. Il a fallu dans certains cas des doses atteignant 1,8 Mégarad. De telles doses répétées plusieurs fois provoquent des altérations profondes des propriétés physiques du papier.

Néanmoins on peut déjà envisager dans l'état actuel de nos connaissances, des traitements expérimentaux de lots d'objets constitués uniquement par des bois non revêtus. Ces traitements seront destinés à nous permettre d'étudier un certain nombre de problèmes annexes, transport, emballages, assurances, etc..., en ayant comme objectif la détermination précise du prix de revient d'un tel traitement. Il apparait important de signaler à ce propos qu'étant donné la grande pénétration du rayonnement γ , le traitement de destruction d'insectes peut s'effectuer à l'intérieur même de l'emballage de transport; notons également, en passant, que dans le cas des musées ethnographiques propres, recevant chaque année des lots plus ou moins importants d'objets nouveaux, l'utilisation du rayonnement γ pour la désinsectisation systématique des nouvelles acquisitions permettrait de réduire considérablement les frais de sauvegarde de l'ensemble des collections.

C. L'imprégnation des bois.

Des travaux importants menés, aux Etats-Unis, par l'Université de West Virginia et le laboratoire national de Brookhaven ont montré tout l'intérêt qu'il pouvait y avoir à remplir la quasi-totalité des vides du bois par un monomère plastique polymérisable. Ces études, conduites avec un objectif essentiellement industriel, peuvent trouver un écho très favorable dans le cas de l'imprégnation des bois anciens. En effet, non seulement les propriétés mécaniques sont améliorées, mais la résistance aux intempéries ou à l'usure est également très augmentée, tout en maintenant l'aspect inchangé.

La méthode consiste à mettre l'objet dans un récipient de taille appropriée, à créer un vide partiel (environ 10 mm Hg) pendant quelques heures, puis à remplir cette cuve par le monomère soumis ensuite à une pression de quelques Kg/cm^2. Après un temps variable de l'ordre de 5 à 15 heures, l'excédent de monomère est renvoyé au stockage, la cuve ouverte et l'objet transporté dans une cellule d'irridiation où il est soumis à une dose variable selon le monomère employé. Il semble préférable d'utiliser la polymérisation par influence du rayonnement γ plutôt qu'une méthode utilisant un catalyseur pour éviter tout traitement chimique du monomère employé et pour pouvoir plus facilement contrôler l'élévation de température liée à la réaction exothermique de polymérisation. En effet, la vitesse de cette réaction étant liée au débit de dose reçue, il suffit dans le cas d'un échauffement trop important d'augmenter la distance source-objet pour réduire à la fois le débit de dose, la vitesse de polymérisation, et donc l'échauffement. Cette souplesse est un des grands avantages de l'utilisation du rayonnement pour des objets non industriels, pouvant être fragiles.

De plus, la dose de polymérisation des monomères les plus courants étant de l'ordre de 2 Mégarad entraine donc pratiquement la stérilité interne des objets limitant ainsi les risques d'actions ultérieures de champignons ou de bactéries.

Les travaux déjà cités ayant un objectif industriel, le choix des monomères a été très fortement influencé par leur coût. Les plus employés ont été : Métacrylate de Méthyle, Styrène-Acrylonitrile, Styrène-Polyester, etc... Nos premiers essais ont porté sur l'utilisation du Métacrylate de Méthyle, dont le polymère (Plexiglass) est bien connu. Les résultats sur des bois très atteints, creusés de nombreuses galeries d'insectes, ont été assez décevants. La tension

de vapeur trop élevée de ce monomère, et sa viscosité trop basse entraînaient, au cours de la polymérisation, un drainage des parties les plus poreuses, donc les plus fragiles. On aboutissait à ce paradoxe : avoir consolider les parties solides, sans renforcer les parties les plus fragiles. De plus, le Métacrylate de Méthyle s'est révélé un bon solvant des peintures! Nous nous sommes alors orientés sur l'utilisation d'un mélange de styrène et de polyester (A 228 de Rhône-Progil) assez fluide pour donner une bonne pénétration, mais ayant une tension de vapeur beaucoup plus faible. Les résultats obtenus sur des bois, très altérés, ont été excellents.

Il est certain que les résultats encourageants obtenus avec ce mélange pourraient vraisemblablement être encore améliorés en utilisant d'autres produits d'imprégnation. Un mélange idéal aurait à notre avis les caractéristiques suivantes :

- Une viscosité relativement élevée (quelques dizaines de centipoises).
- Une température d'ébulition la plus haute possible, de façon à avoir une tension de vapeur très basse à la température ambiante.
- Un pouvoir réticulant élevé, permettant d'obtenir des polymères à haut poids moléculaire.
- Un effet solvant, en particulier sur l'huile de lin, le plus faible possible.
- Son polymère doit avoir une excellente résistance au feu, pour éviter l'adjonction d'additifs de prix élevé.
- Il doit avoir de plus une très grande inertie vis à vis de l'eau ou de l'humidité.

- Le polymère doit être soluble dans un solvant courant inoffensif pour les revêtements. Ce solvant pourrait être à la rigueur le monomère lui-même. L'objectif étant de pouvoir extraire le polymère au moins dans les parties superficielles des objets.
- Bien que le matériau imprégné offre une excellente protection contre les rayonnements ultra-violets il importe de choisir un imprégnant dont le polymère soit assez inerte vis à vis des U. V.
- Le coefficient linéaire de dilatation thermique doit être assez proche de celui du bois, ou bien le polymère doit présenter une certaine souplesse.

Il n'est pas certain que l'on puisse trouver dans les produits couteux l'ensemble de toutes ces qualités, mais le prix du traitement est suffisament faible pour que l'on puisse envisager d'étendre le choix vers des monomères moins courants et donc plus chers. La recherche d'un tel mélange idéal sera notre objectif pour les prochains mois.

Dans l'état actuel des choses, on peut tout de même envisager, à titre expérimental des traitements sur les bois naturels non revêtus, sur les bois dorés, ou avec des précautions sur des bois recouverts de peinture utilisant des liants autres que l'huile de lin.

Il faut encore signaler que le matériau imprégné présente une très grande résistance au vieillissement ainsi qu'à l'action des insectes. La résistance aux champignons peut être un peu faible, les facultés d'adaptation de ces organismes leur permettant de vivre sur les matières plastiques. Toutefois, cette action ne pourrait être qu'une action superficielle, facile à déceler, et assez rare pour des objets conservés dans des conditions normales.

D. Conclusion

L'utilisation du rayonnement γ apporte donc deux solutions à la conservation des bois. La première, que l'on pourrait qualifier de passive offre le moyen de stopper des détériorations dans des conditions économiques très bonnes et sans danger. La seconde, que l'on pourrait qualifier d'active, assure la transformation du bois en un matériau beaucoup plus résistant et dans des conditions économiques abordables. Si cette dernière méthode a encore besoin de beaucoup d'étude, en particulier dans le domaine des matériaux revêtus, elle constitue sans aucun doute la voie vers de très grandes possibilités d'emploi pour la conservation des biens culturels.

Le grand soleil rouge de terreur, que nous avons évoqué au début de cet exposé, devient alors le soleil de l'espoir.

- o O o -

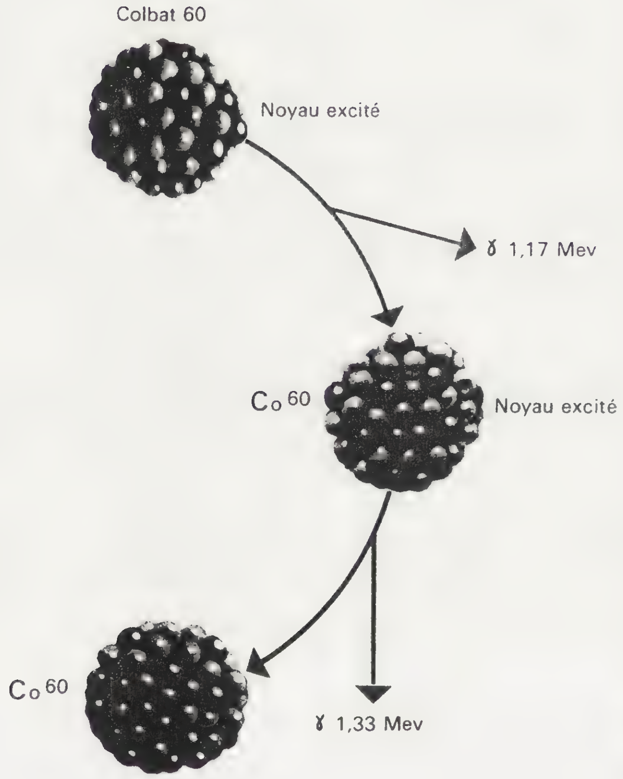
Nous tenons à remercier ici la rédaction de la Revue du Ministère du Développement Industriel et Scientifique pour nous avoir autorisé à publier dans ce rapport les photographies extraites de leur publication.

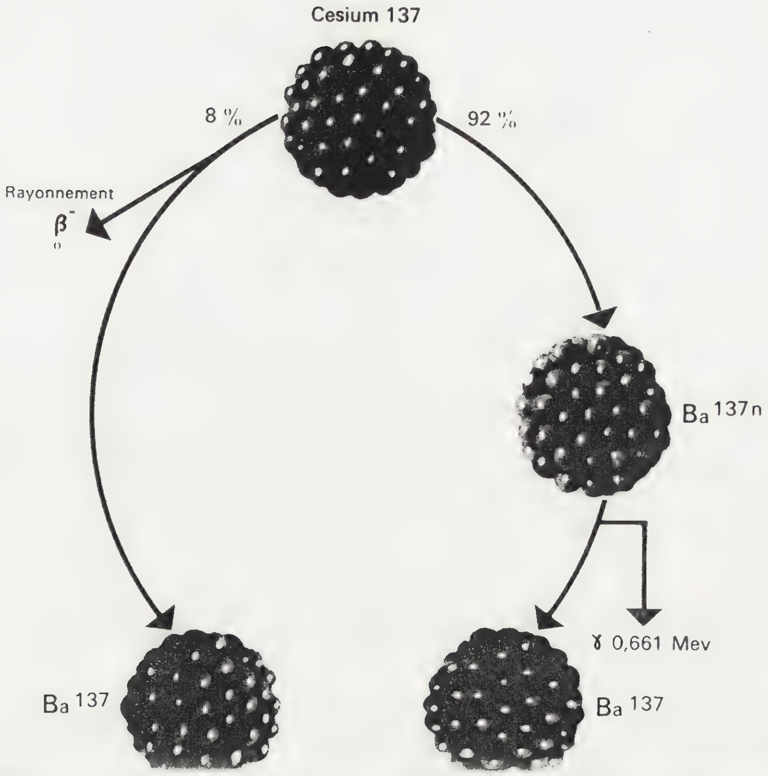
Erratum

Le Coblat 60 donne après émission de deux photons γ et d'un électron de 0,31 Mev du Nickel 60 ($_{28}N_i^{60}$).

ÉMISSION D'UN RAYON GAMMA

ci-contre, à partir de Cobalt 60
ci-dessous, à partir de Cesium 137


Colbat 60
Noyau excité
γ 1,17 Mev
Co 60
Noyau excité
Co 60
γ 1,33 Mev


Cesium 137
8 %
92 %
Rayonnement
β⁻
Ba 137n
γ 0,661 Mev
Ba 137
Ba 137

Source de cobalt 60 dans sa piscine de stockage utilisée pour les irradiations de biens culturels

Parquet du musée Stendhal à Grenoble après traitement et repose

ANNEXE

RAPPEL DE QUELQUES NOTIONS DE PHYSIQUE DU RAYONNEMENT.

A. Interaction des photons avec la matière.

Cette interaction peut s'effectuer suivant plusieurs modes, dépendant de la nature du milieu considéré et de l'énergie des photons. Dans le domaine d'énergie qui nous intéresse, il faut considérer principalement l'effet Compton et l'effet photoélectrique. Pour être tout à fait rigoureux, il faudrait également tenir compte de la création de paires d'électrons.

1. Effet Compton.

L'effet Compton est l'interaction d'un photon avec un électron libre avec transfert à ce dernier d'une partie de l'énergie du photon. Des relations définissent l'énergie du photon secondaire ou de l'électron en fonction de l'angle de diffusion (angle entre la direction du photon incident et celle du photon secondaire).

2. Effet Photoélectrique.

Lorsqu'un noyau intervient dans l'interaction d'un photon et d'un électron, la conservation de l'énergie et du moment du photon incident peut être assurée par le recul du noyau atomique. L'électron est alors éjecté de l'atome avec une énergie représentant presque toute l'énergie incidente (il n'y manque que l'énergie de liaison de l'électron). Comme

pour l'effet Compton on peut déterminer une section efficace ou probabilité d'apparition de l'effet photoélectrique mais elle est plus accessible à l'expérience qu'au calcul.

3. Création de paires.

Lorsqu'on a affaire à des photons d'énergie supérieures à 1,02 MeV, on voit apparaître un nouveau type d'interaction : la création d'un ensemble de deux électrons de charges électriques opposées : e^+ et e^- dont l'énergie totale au repos est de 1,02 MeV. Cependant pour l'énergie moyenne du Cobalt 60, (1,17 et 1,33 MeV) la section efficace de création de paires peut être considérée comme négligeable.

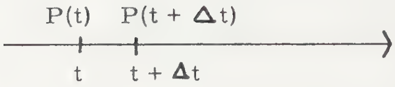
4. Section efficace totale.

La somme des sections efficaces ramenées à 1 cm^3 de matière correspond à la probabilité pour un photon incident de subir dans ce volume une des interactions envisagées. Elle est appelée coefficient d'atténuation μ du rayonnement. Ce coefficient étant directement lié au nombre de noyaux et d'électrons présents dans le volume, on conçoit que pour un matériau donné, on ait $\frac{\mu}{\rho} =$ constante (ρ = densité du matériau). On constate même que $\frac{\mu}{\rho}$ ne varie que lentement lorsqu'on passe d'un élément à l'autre puisque tous les éléments présentent à peu près le même nombre d'électrons par gramme et que ceux-ci jouent un rôle important dans l'atténuation (effet Compton). On définit aussi une section efficace d'absorption μ_a qui est le produit de μ par la fraction de l'énergie cédée, en moyenne, au milieu (aux électrons et aux noyaux).

B. L'atténuation des photons.

1. L'atténuation des photons primaires.

Considérons la trajectoire d'un photon dans un milieu homogène infini et soit P(t) la probabilité pour que le photon parvienne jusqu'au point d'abscisse t sans avoir subi d'interaction. La probabilité pour qu'il subisse une interaction dans le parcours Δt sera $\mu \Delta t$. La probabilité pour qu'il ne subisse pas d'interaction sera $1 - \mu \Delta t$.



On peut donc écrire :

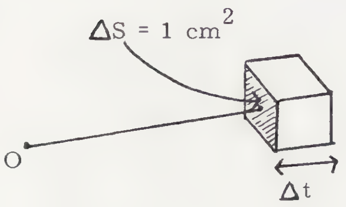
$$P(t + \Delta t) = P(t) \cdot (1 - \mu \Delta t)$$

$$dP = - P \mu \, dt$$

et en intégrant :

$$P = e^{-\mu t}$$

Si maintenant nous considérons un photon émis à partir d'une origine O d'une façon isotrope, la probabilité pour qu'il traverse l'élément unitaire placé à une distance r sera :



$$P = \frac{1}{4\pi r^2} \quad e^{-\mu t}$$

et le flux de photons émis par une source de S photons par seconde sera au point P :

$$\phi \quad \frac{S}{4\pi r^2} \quad e^{-\mu t}$$

2. Les photons secondaires et le build-up.

La loi d'atténuation des photons primaires est donc simple. Mais la plupart des photons subissant une interaction donnent naissance, par effet Compton, a des photons diffusés secondaires. Il n'est pas possible de faire un calcul rigoureux du flux en tenant compte de ces photons secondaires.

Cependant, dans beaucoup de cas, on a une approximation suffisante pour le flux incident en calculant le flux de photons non diffusés et en appliquant un terme correctif appelé coefficient d'accumulation (Build-up).

3. L'énergie absorbée.

Si on néglige le parcours des électrons secondaires relativement petit, l'énergie absorbée ne dépend pas de la direction des photons incidents. La grandeur représentative de cette énergie absorbée au point d'interaction d'un photon, est le Kerma (Kinetic Energy Release in Material) ou énergie cédée à un gramme de matière.

$$K = \int_{o}^{E\ max.} N_o\,(E)\ .\ \frac{\mu_a\,(E)}{\rho}\ .\ E\ .\ dE \quad \text{exprimé en MeV/g. sec.}$$

avec N_o (E) = nombre de photons d'énergie E par cm^2 et par seconde.

4. Equilibre électronique.

Si, dans un volume irradié infinitésimal, le nombre d'électrons secondaires entrant dans le volume à chaque seconde est égal au nombre d'électrons secondaires quittant ce volume, on dit qu'il y a équilibre électronique. Dans ce cas, l'énergie cédée par les électrons au milieu (ou dose absorbée) qui apparaît finalement sous forme d'effet chimique ou de chaleur, est égale à l'énergie cinétique crée, donc au Kerma. Lorsqu'on est loin des limites de deux milieux, la condition d'équilibre électronique est à peu près réalisée car le Kerma ne varie que lentement. Près des limites de deux

milieux, on peut commettre des erreurs assez importantes en assimilant la dose absorbée au Kerma.

5. Unités relatives au rayonnement.

L'énergie des photons est donnée en MeV

L'énergie absorbée est donnée en Rad

1 MeV = 1,6 10^{-6} erg.

1 Rad = 100 erg/g.

1 MeV/sec. = 1,6 10^{-13} Watt

1 Curie = 3,7 10^{10} désintégrations/sec.

C. Le calcul des doses.

1. Cas d'une source ponctuelle.

En tenant compte du facteur d'accumulation (Buil-up) le flux de photons d'une source ponctuelle sera :

$$\phi = S \cdot \frac{1}{4\pi r^2} \cdot e^{-\mu t} \cdot B(\mu t)$$

Les valeurs de B (μ t), facteur d'accumulation, sont données par des tables ou peuvent être mise sous la forme du genre :

$$B(\mu t) = A\, e^{-\alpha_1 t} + (1 - A)\, e^{-\alpha_2 t}$$

ou A, α_1, α_2, sont des constantes dépendant du matériau considéré.

Lorsqu'on ne se trouve pas en milieu infini on montre que les trois premiers termes : S, activité de la source, $\frac{1}{4\pi r^2}$ distribution spatiale et atténuation des photons primaires sont valables à condition d'écrire

$$e^{-\sum_{1}^{i} \mu_i t_i} \quad \text{au lieu de } e^{-\mu t}$$

2. Cas des sources complexes.

Dans la plupart des cas, les sources ne se présentent pas sous une forme suffisamment simple et la cible irradiée non plus. On est obligé d'avoir recours à un calcul numérique point par point. Cette méthode est en outre nécessaire lorsque les produits irradiés se déplacent dans la zone d'irradiation, ce qui est généralement le cas. Ces calculs sont our la plupart effectués à l'aide d'ordinateurs.

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ICOM COMMITTEE ON CONSERVATION

MADRID MEETING
OCTOBER 2 - 7, 1972

RADIOSTERILIZATION OF WOODEN ARTICLES OF ART AND MUSEUM OBJECTS

BY

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8981/10

In restoring wooden sculptures or ornamental carvings, or polychromatic paintings on a wooden base, the step in the overall conservation cycle that presents a major problem are sterilization procedures. Conventional methods of sterilization are laborious and time-consuming. In addition, making use of toxic substances, they involve a health risk to the restorer.

To avoid these drawbacks, it is evidently necessary to screen for and develop modes of sterilization that are rapid, simple, and safe. Radiosterilization appears to satisfy these requirements. In the object being sterilized, rises in temperature are negligible and discernible physical or chemical changes only occur where radiation doses used exceed by several factors the level needed to destroy invading microorganisms and pests. One limitation that should be considered is that, at a dose above $5x10^5$ rad, colour values may be slightly altered in light-tinted coatings of painted objects. Therefore, preliminary radiation experiments have to be performed to investigate shade modifications in polychromatic coatings on wooden objects and define optical sterilization conditions for a given type of sample.

It was the aim of the present work to study radiosterilization as applied to treatment of items of historical interest or esthetic merits.

Materials and Methods

1. Radiation conditions

Irradiations were carried out on a cylindrical ^{60}Co irradiator RHM-Gamma-20, produced in U.S.S.R., of total activity about $1,2x10^4$Ci.

For dose-rate distribution measurements of the gamma-ray field Fricke ferrosulfate dosimeter (10) was used. A dose indicator Megaray-Print, produced in Hungary, was provided for each sample during irradiation.

2. Microbiological assays were carriedout on naturally contaminated wood samples. Preliminary experiments provided information on individual radiosensitivity of selected fungi and spore-forming bacteria, common for such samples. Suppression of fungal or bacterial growth, as evidenced by failure of colony formation, was the criterion for a successful sterilization.

To determine initial contamination in wood samples, the following procedure was used. Wood material, weighing 200± 20 g, immersed in 200 ml. of saline in a 1 L beaker, was agitated 30 min. by shuttle device. After 24 hr of incubation at 2° C, the 30 min. agitation was repeated. Washings were then collected and serially diluted by transferring appropriate aliquots to conventional agar medium. For each sample, six seedings were made and kept in thermostate, three of them at 37°C and three at 22°C, for a period of 72 hr. Records were made of the number of oolonies formed and total amount of microorganisms per sample was estimated.

An alternative procedure, intended to provide rapid information on initial contamination, omitted one 30 min. agitation and the incubation at 2°C, the rest of the steps being as in the first alternative.

Analysis of the results obtained indicated the first alternative to be definitely superiour as to accuracy and completeness of data on initial sample contamination. It was therefore preferred.

The second alternative could be useful if restricted to cases where rapid screening for types and amounts of contaminating microorganisms is required.

Radiosensitivity was individually investigated for two commonly encountered fungal species CONIOPHORA CEREBELLA and MERULIUS LACRYMANS as well as a spore-forming bacterial species BACILLUS SUBTILIS.

Growth media. C.CEREBELLA and M.LACRYMANS were cultivated on Sabourcau's minimal ager. For B.SUBTILIS, conventional calf meat infusion agar was used.

Microorganisms suspensions. Five agar surfaces in Petri dishes were inoculated by means of a glass spatule with either C.CEREBELLA or M.LACRYMANS. Fourteen days of cultivation at 22°C resulted in dense growth and maturing of spores. Microorganisms were harvested by washing with saline and using a metallic spatule, then hand-mixed for 15-20 min. and filtered through sterile glass wool. The resulting filtrate represented an uncontaminated suspension of 10^6 spores/ml. These suspencions were kept in a refrigerator until use.

B. SUBTILIS suspensions of 10^9 spores/ml were prepared by standard techniques.

Irradiation. 1 ml volumes of each spore suspension type, pH=7, were irradiated in $15^0/15$ mm thin-walled tubes. Temperatures during exposure varied between 15 and 18°C.

Wood samples to be radiosterilized were placed in sealed polyethylene bags and tested directly postradiation for residual contamination.

ssessment of radiation effect.Serial dilutions were made of each mple by seeding appropriate aliquots on Saboureau agar for .CEREBELLA and B.SUBTILIS. Three seedings of each dilution were ultivated for 7 days at 22°C, for C..CEREBELLA and M.LACRYMANS, or t 37°C, for B.SUBTILIS. Colonies formed were scored and amount of pores per sample estimated. The figures given are the mean of three ndependent investigations.

To determine residual contamination of irradiated wood sam- les, identical procedures were used as for initial contamination.

. RADIATION DISINFESTATION OF WOOD.

Wood samples attacked by pests typical for this country - NOBIUM PUNCTATUM, XESTOBIUM RUFOVILLOSUM, ANORIUM PERTINAX, YLOTRUPES BAJULUS - were subjected to radiation disinfestation. Two dose levels were employed, 60 Krad or 140 Krad. To substan- tiate the effect obtained, the samples were carefully sliced and xamined at 10-fold magnification for dead or surviving insects. No investigation was made of gamma-ray effect on eggs as subsequent preventive treatment applied directly postradiation ruled out larvae pupation exclusion and resulting penetration of cellulose.

4. Materials and Methods for Assaying optical stability of common binders and pigments.

The majority of 18 - 19 century wood carvings of Bulgarian origin possess a polychromatic coating. In addition, religious paintings dating from adoption of christianity up to the 20th century have already been executed on a wooden base. It was thus necessary to test a total of 11 binding agents and 17 pigments for optical resistance to ^{60}Co gamma rays.

Radiation experiments were performed on two types of samples (i) small fragments of original paintings (debris of an unrestorable late 19th century icon); and (ii) specially prepared wood samples coated with traditional or contemporary pigments and varnishes.

The original painting was samples by removing from the wood base portions of the pigment coating, along with ground coating (carbonate ground+animal glue as binder), or irregular shape and a mean area of 0,5 cm^2. Colours in the samples investigated included: golden leaf; brown (ferric oxide); ochre (ferric oxide); green (earth); incarnat; ; black (plant), red (cinnabar + ferric oxide); white (white lead)); grey (black and white).

None of the colours, apart from white, was a pure pigment. Fragments were halved to ensure a reference for postradiation comparison. This was done visually by three experts, painters whose vision had been proved normal.

To ensure reliability of results, experiments were carried out with specially prepared coniferous wood 10x20x2 on samples. These were coated with lime-carbonate white ground plus one of several binders, the procedure being repeated until a film of sufficient thickness was formed. When completely dried, half of the surface was overlaid with a pigment coating, containing the the bindier used for the ground in the specific case. One pigment was used for all samples - natural ochre, light -resistant and of a rather light tint so that any [illegible] easily be detected. Prior to irradiation, each sample was halved

longitudinally to obtain identical fragments, equal parts of which were coated either with binder or binder+pigment. One half-sample was irradiated, the other serving as control.

The following binding agents were used: linseed oil;wax-egg emulsion; mastic in turpentine; dammar in turpentine; colophony in turpentine; a 10 % polyvynil-acetate emulsion Movilit-D-50; 8% polyvinylalcohol-Gelvatol 40 in alcohol and water; 10% acrylate emulsion Primal AC-33, in toluene; 8" polyvinylacetateVinavil K-60, in toluene and acetone; silicone emulsion.

To explore radioresistance of individual pigments, a second series of experiments was carried out with wood samples ground pigment coatings; ochre, light; ochre, red; ochre,holden; sienna, natural; sienna, burnt; umber, natural; umber, burnt; mars,light-brown; mars, dark brown; emerald green; cobalt; ultramarine, cadmium yellow; cadmium red, light; cadmium, red dark; craplack; plant black.

Two radiation dose levels, 140 Mrad or 4 Krad, were employed with each of the samples investigated.

5. Postradiation chemical preventive treatment

Chemical protection against deteriorating effects of insect, fungal, mould or bacterial attack on wood is achieved by injecting exit holes with "durvoconserveer" (a wood preservative), repeating the procedure from 2 to 4 times. When treating works of art by injection, care should be taken to prevent penetration of the coating by the preparation used, though antiseptics and solvents contained in it are relarively safe. Depending on characteristics of the work to be treated (extent ofdeterioration,

type of wood, presence of coatings, esthetic value, etc.), low pressure may be used in the procedure. Autoclaving or immersion are discouraged.

In high relative humidity environments, preventive treatment is carried out with "Groundbezeer". Where conditions favouring development of wood-attacking pests prevail, treatments are to be repeated according to the restorer's judgement. the rotection thus achieved is more reliable and lasting.

Disrupted coatings and wood are stabilized and face surfaces given antistatic treatment in compliance with formulas and procedures, adopted by the National Institute for Cultural Property. (1,2,3).

Results

Ireradiation contamination of wood samples was found to equal $2,8\times10^5$ microorganisms per gram (fungi and moulds, 79,5%; spore forming microorganisms, 20,5 %). This microflora was complctely destroyed by either of the two radiation doses employed (2,5 or 3,2 Mrad).

Results obtained on individual radiosensitivity of common fungi and spore-forming bacteria are summarized in Table 1 and Figures 1 and 2. It will be seen that B.SUBTILIS markedly differs from both fungi species, CONIOPHORA CEREBELLA and MERULIUS LACRYMANS, in sensitivity to 60_{Co} gamma rays.

D_{10} for B.SUBTILIS was found to equal 26 Krad. Basing on this finding, it was estimated that for an initial microorganism contamination of 10^{12}/ml of washings, which is a rarity, a sterilization dose of 310-320 Krad would be adequate.

In Table 1 and Figure 1, radioresistance is not only shown to be definitely higher in fungi compared to B.SUBTILIS, but also to differ between fungi . D_{10} values derived from the curves in Figure 2 for C.CEREBELLA and M. LACRYMANS equal 80 and 60 Krad at initial spore concentrations of 8.10^6 and 3.10^6 per ml. respectively.

From the data presented, it may readily be estimated that to sterilize objects contaminated by C.CEREBELLA or M.LACRYMANS, at 10^{12} spores/ml, a dose of 960 or 720 Krad, respectively should well be sufficient.

In the first experimental series with 60 Krad, aimed at radiation disinfestation, it was found that not all of wood - pest larvae are being destroyed. A second series of irradiations was therefore performed at a dose exceeding 100 Krad, i.e. at a level that is lethal to any larva or nature organism of tje species hitherto investigated, excepting HYLOTRUPES BAJULUS.

Tables 2 and 3 summarize data on visually detectable changes in samples specially prepared to test optical resistance to 60_{Co} gamma rays. In fragments of the original painting exposed to 2,5:3,2; or 4,5Mrad, no visually discernible difference from unirradiated controls was observed.

Conclusions

1. The results obtained indicate that in many cases of attack, namely by common fungi or bacteria, radiosterilization of wood may successfuly be applied as part of the overall conservation cycle.

2. Insect irradication was readily achieved at radiation do-

[illegible] that are safe to coloured works of art.

3. Wooden objects of historic or esthetic value were sterilized at the selected radiation doses, 2,5, or 3,2 Mrad, which exceed by several factors the dose found, under experimental conditions, to be lethal to common microorganisms. A wide margin of safety is thus ensured in radiosterilization of objects of such type.

4. Radurisation is regarded as an efficient and promising means for treatment of cellulose attacked by insect pests or microorganisms.

ABLE 1

ON-[illegible] DECLINE IN AMOUNT OF VIABLE SPORES EXPOSED TO

^{0}Co GAMMA RAYS.

Dose	AMOUNT OF MICROORGANISMS PER MILLILITER					
KRAD	C. CEREBELLA		M. LACRYMANS		B.SUBTILIS	
	N	N/No	N	N/No	N	N/No
5	Ø	Ø	Ø	Ø	4.32.10^{7}	3.85.10^{-1}
30	1.22.10^{6}	1.50.10^{-1}	7.56.10^{5}	2.52.10^{-1}	9.10.10^{6}	8.13.10^{-2}
60	9.84.10^{5}	1.20.10^{-1}	2.68.10^{5}	9.00.10^{-2}	5.20.10^{5}	4.64.10^{-3}
90	6.80.10^{5}	8.40.10^{-2}	8.20.10^{4}-	2.75.10^{-2}	4.10.10^{4}	3.66.10^{-4}
150	7.40.10^{4}	9.10.10^{-3}	7.00.10^{3}	2.33.10^{-3}	2.30.10^{2}	2.05.10^{-6}
300	4.75.10^{3}	5.90.10^{-4}	1.00.10	3.30.10^{-6}	-	-
600	-	-	-	-	-	-
900	-	-	-	-	-	-
1500	-	-	-	-	-	-
0	8.11.10^{6}		3.00.10^{6}		1.12.10^{8}	

Ø - not investigated

- = failure of growth

TABLE 2

DOSE DEPENDENT ALTERATIONS OF BINDERS EXPOSED TO $^{60}C_o$ GAMMA RAYS

BINDER	CHANGE OF DOSE OF Mrad		
	0.15	0.5	4.0
Wax-egg emulsion	(-)	(-)	(-)
Linseed oil	(-)	(-) (+)	[illegible]
MASTIC	(-)	(-)	(++)
dammar	(-)	(-)	(++)
Colophony	(-)	(-)	(+++)
Movilit D-50	(-)	(-)	(+++)
Gevatol 40-20	(-)	(-)	(+)
Primal AC-33	(-)	(-)	(++)
Paraloyd B-72	(-)	(-)	(++)
Vinavil K-60	(-)	(-)	(-) (+)
Silicone emulsion	(-)	(-)	(++)

(-)	No change
(+)	Shading and cooling
(++)	Moderate shading and cooling.
(+++)	Pronounced shading and cooling
(-) (+)	Very mild shading and cooling

TABLE 3

PIGMENT CHANGES FOLLOWING TREATMENT WITH 4,0 Mrad of ^{60}Co Gamma rays

PIGMENT	CHANGE
Light ochre	No change
Red ochre	No change
Golden ochre	Slightly lighter
Sienna natural	Slightly lighter
Sienna burnt	No change
Umber natural	No change
Umber burnt	No change
Mars light brown	Slightly lighter
Mars dark-brown	Slightly lighter
Ultramarine	Slightly lighter
Cobalt	No change
Emerald green	No change
Cadmium gelb	Slightly lighter and cooler
Cadmium red light	No change
Cadmium red dark	No change
Kraplack	No change
Plant black	No change

REFERENCES

1. Mikhailov Anton: Conservation of wood works of art in Bulgaria, 1970, New York Conference of Stone and Wooden Objects.

2. Mikhailov, Anton, Gaidarkova Lydia: Wood pests in our Homes and the Building Industry, Publ . Zemizdat, Sofia, 1958.

3. Mikhailov Anton: Theoretical considerations in treatment and protection of old structures and wooden works of art. Darvoobrabotvashta i Mebelna Promishlenost (Sofia), No. 1,1970.

4. Mikhailov Anton: Conservation and Sterilization of various wooden works of art in Bulgaria, Sbornik Soobshchenyi (Moscow), No. 6, 1966.

5. Mikhailov Anton: Treatment and protection of furniture against wood-attacking beetles. Darvoobrabotvashta i Mebelna Promishlenost (Sofia), No. 7, 1968.

6. Forsidin A.G.: Ionizing Radiation Effects on Cellulose and its Components. Publ. Goslesbumizdat, Moscow,1961.

7. Brommel N.S.: The conservation of interior wood-work particularly furniture. The International Council of Museums, Paris, 1963.

8. Werner A.E.D: Conservations of fixed wooden structures. The International Council of Museums, Paris, 1963.

9. Kalninsh A.Ya.: Cellulose Conservation, Publ. Goslesbumizdat, Moscow, 1968.

10. Sharov P.G., Karadjov A: Study of dose distribution in a cylindrical gamma-irradiator (in press).

Fig. 1: Dose Dependence of the Ratio N/N_o. Abscissa, dose in kilorad; ordinate , N/N_o (N_o, initial number of microorganisms per unit of volume; N, number of surviving microorganisms per unit of volume).

Fig. 2: Dose dependence of survival per unit of volume (survival curves). Abscissa, dose in kilorad; ordinate, number of microorganisms per milliliter

D_{10} values (10-fold decrease in survival)

1. ○-----------○ C.Cerebella
2. △-----------△ M.Lacrymans
3. □ ----------□ B.Subtilis

1. ○----------○ ∼80 Krad
2. △---------△ ∼60 Krad
3. □ --------□ ∼26 Krad

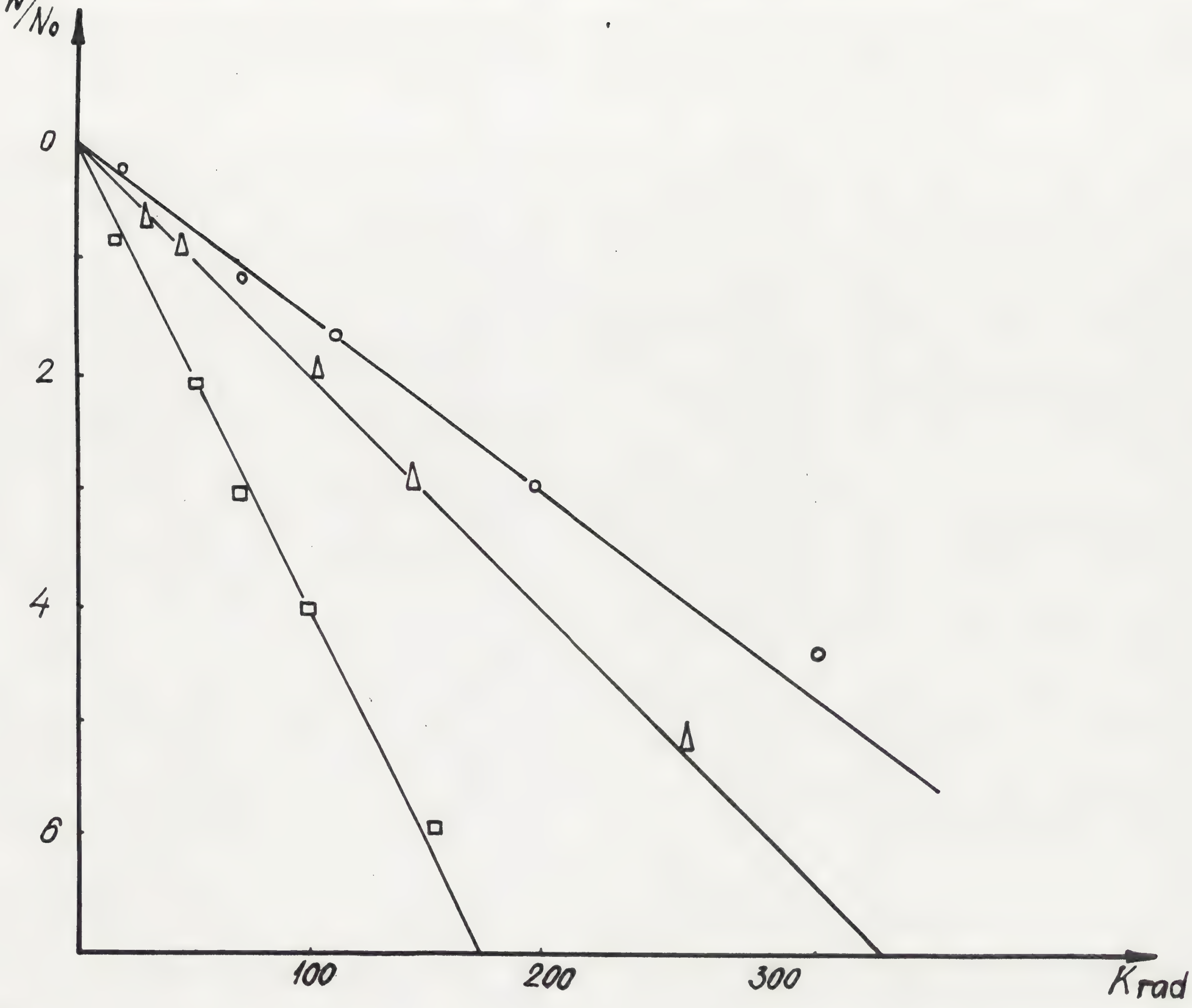

fig. 1

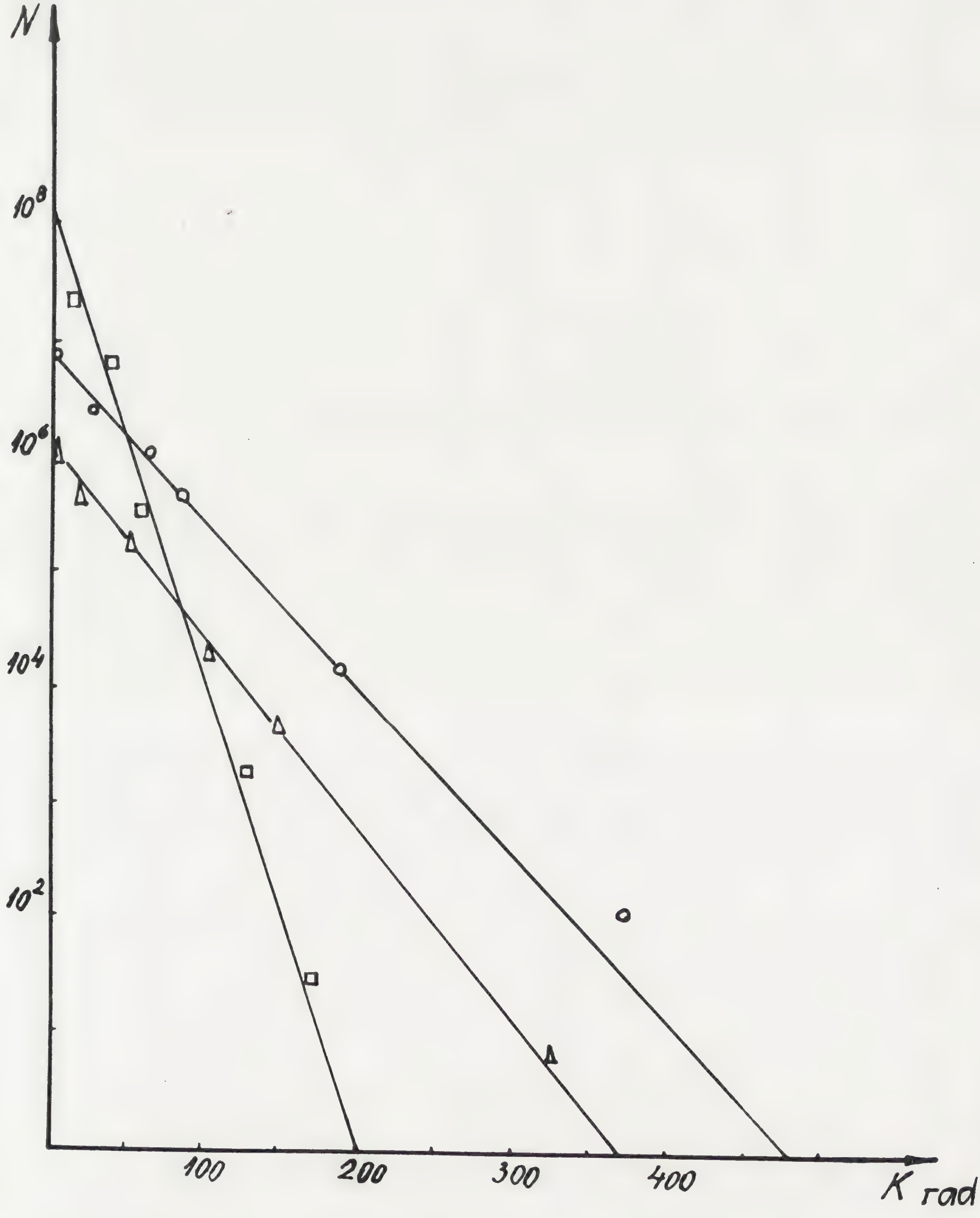

fig. 2.

[illegible] /5

ARTIFICIAL AGEING OF YARNS IN PRESENCE AS WELL AS IN ABSENCE OF LIGHT AND UNDER DIFFERENT ATMOSPHERIC CONDITIONS

IV

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IV

PRELIMINARY RESULTS

For more details on the working-programme see the foregoing interim reports (1), (2), (3).

1. AGEING METHODS

Ageing of the textile materials was mainly performed by the following methods :

method	light source	temp. °C	effective rel.hum. %	atmosphere
1	-	55	10	ambient
2	-	55	90	ambient
3	TL 57	39	22	ambient
4	TL 57	45	22	purified
5	-	45	22	purified
6	TL 57	45	22	purified + ca. 5 ppm NO_x
7	-	45	22	purified + ca. 5 ppm NO_x
8	TL 57	45	22	purified + ca. 20 ppm SO_2
9	-	45	22	purified + ca. 20 ppm SO_2
10	TL 57	45	22	purified + ca. 5 ppm NO_x + ca. 20 ppm SO_2
11	-	45	22	purified + ca. 5 ppm NO_x + ca. 20 ppm SO_2
12	TL 57	45	22	purified + ca. 0.3 ppm O_3
13	-	45	22	purified + ca. 0.3 ppm O_3
14	TL 57	45	< 0.05	purified
15	TL 57	45	22	oxygen-free nitrogen (O_2-conc. < 1 ppm)

The materials were degraded by these ageing methods for different periods of time, and after each period the properties described in METHODS OF TESTING were determined. In our experiments the longest period of time was five years.

Methods 1 and 2 were performed in climate cabinets, the experiments

in presence of light (methods 4, 6, 8, 10, 12, 14 and 15) in irradiation apparatus as described in the first Interim Report (1). Methods 5, 7, 9, 11 and 13 were performed in apparatus similar to the irradiation apparatus, but without a light source. The concentrations of SO_2 and NO_x were chosen at a value of ca. 50 times the highest ever measured values (24 h average value) of these gases in an industrial area (Rotterdam, 1965). The ozone concentration used was about as high as the highest measured value in this area.

2. AGEING OF CELLULOSE YARNS

2.1. Materials

a. Cotton yarn, Peruvian cotton, combed, 20 tex.
   1. Raw
   2. Bleached
   3. Scoured, mineral khaki dyed

b. $\frac{1}{4}$-bleach linen yarn, 50 tex.

2.2. Methods of testing.

a. Determination of the breaking load.
   1. of single yarns at gauge lenght of 500 mm
   2. of bundles of yarns at gauge lenght of 0 mm

b. Determination of the degree of polymerization (DP).
   1. Viscosity - average DP ($\overline{DP}_v$) by way of the viscosity of a solution of a derivative of cellulose (cellulose trinitrate in ethylacetate)
   2. Number - average DP ($\overline{DP}_n$) by way of the osmotic pressure of a solution of a derivative of cellulose (cellulose trinitrate in either ethylacetate or acetone)

The viscosity - average DP is always larger than the number-average DP.

The degree of polymerization decreases during degradation. The difference between the reciprocal DP´s at two stages of one degradation process is a measure for the number of chain scissions in the cellulose that have happened during the period of degradation. For the sake of convenience this difference is multiplied by 10,000, giving the grade of scission (g.s.).

In formula :

$$g.s. = \frac{10,000}{DP_2} - \frac{10,000}{DP_1}$$

wherein DP_1 = DP before degradation

DP_2 = DP after degradation

c. Analysis of the functional groups in cellulose.

1. Determination of acidic groups by reaction with the alkaline dyestuff methylene blue. The decrease of the methylene blue content of the test solution was determined colorimetrically.
2. Determination of reducing groups by reaction with 2,3,5 - triphenyltetrazoliumchloride. The quantity of the formed red coloured compound triphenylformazan was determined colorimetrically.
3. Infrared analysis.

d. Analysis of gases generated during the ageing of cotton and linen.

1. Determination of CO_2 by formation of carbonate
2. Determination of CO by reduction of I_2O_5 to I
3. Gaschromatography.

2.3. Discussion of the results.

a. To characterize the environments of degradation we tried to assess a coefficient of degradation (c.d.) for each ageing method investigated. This c.d. should be inversely proportional to the rate of degradation measured.

Unfortunately it appeared to be impossible to assess this coefficient unambiguously.

b. Native cellulosic materials are not to be regarded as consisting of cellulose only. The composition of the material and especially the structure on the molecular and supramolecular scale is very important. The different behaviour of raw cotton and of bleached cotton on irradiation in air polluted with SO_2 and NO_2 is particularly surprising. (table 2.1.)

c. The degradation of cotton cellulose can be considered to be mainly the result of breakages of the macromolecular cellulose chains. Chemical changes have not been detected with the methods 2.2.c and 2.2.d.

The chains are broken at weak and reactive spots. The number of

these spots and their distribution along the crystalline fibrils determine the properties of the fibre to a great extent. We believe these spots are located near chain ends, because chain ends will cause stresses in the bonds of neighbouring chain molecules, resulting in an increase of the reactivity of these bonds. External stresses may also increase the reactivity of the bonds in chain molecules (4).

d. The spectral energy distribution of the incident light has a great influence. (table 2.2.)

e. The rate of degradation during irradiation is proportional to the light intensity which is roughly inversely proportional to the distance between the source of light and the object, when irradiated by fluorescent lamps at short distances.

f. A rise of temperature of the yarns during irradiation with the daylight lamp (from 43° to 57 °C) brought about an increase in the rate of degradation in the order of 30 %, which was much less than had been expected.

g. The rate of degradation during irradiation increases with increasing O_2- content of the surrounding atmosphere. This rate is not proportional to the O_2- concentration, but seems to change linearly with its logarithm (fig. 2.1.).

h. As a general rule it was found that the degree of degradation (expressed as g.s.) caused by a number of factors in conjunction is not equal to the sum of the effects brought about by each of the factors separately (table 2.1.). This is to be expected in the case of light, because of its capacity to activate one or more substances involved in the process of degradation.

i. The investigated circumstances and factors causing degradation can be very roughly placed in the following row of increasing rates of degradation.

No light , climate cabinet , dry atmosphere (55 °C, ca. 10% r.h.)
No light , climate cabinet , wet atmosphere (55 °C, ca. 90% r.h.)
No light , stream of polluted air *(45 °C, ca. 22% r.h.)
Light , purified air , humified (45 °C, 22% r.h.)
Light , purified air , very dry (45 °C, < 0.05 % r.h.)
Light , stream of polluted air * (45 °C, 22% r.h.)

* air containing one or two of the following pollutants :

SO_2 (ca. 20 ppm), NO_x (ca. 5 ppm), O_3 (ca. 0,3 ppm).

j. The rate of degradation during irradiation in purified air (45°C,

22% r.h.) was 100 times the rate of degradation in storage in our physics laboratory (20 °C, 65% r.h. , no light).

k. After a given number of scissions (i.e. at a given g.s.) linen has lost more of its strength than cotton (fig. 2.2.).

l. Khaki mineral dye protects cotton against irradiation (fig. 2.3.). The dye absorbs light, especially light of short wavelengths.

3. AGEING OF WOOL YARNS

3.1. Materials

The wool (Merino type, scoured industrially in a very mild way) was after combing spun to folded yarns of count 25 x 2 tex (Nm 40/2). This yarn was treated in one of the following ways :

1. rinsed with water
2. washed with "natural" soap [1] (anionic), and rinsed
3. washed with Nekanil LS (anionic), and rinsed
4. washed with Nekanil O extra (nonionic), and rinsed
5. washed with Nekanil W extra (nonionic), and rinsed
6. washed with domestic detergent (synergetic mixture + bleach + optical brightener), and rinsed
7. extracted with di-ethyl-ether
8. washed with "natural" soap, treated with acetic acid at pH 5.0, and rinsed
9. idem, idem at pH 3.5, idem
10. idem, treated with formic acid at pH 5.0, and rinsed
11. idem, idem at pH 3.5, idem
12. idem, idem at pH 2.0, idem
13. idem, treated with sulphuric acid at pH 5.0, and rinsed
14. idem, idem at pH 3.5, idem
15. idem, idem at pH 2.0, idem
16. rinsed with water, treated with chrome mordant, and rinsed
17. idem, dyed with fustic, and rinsed
18. idem, dyed with logwood, and rinsed
19. idem, dyed with brasil wood, and rinsed
20. idem, dyed with alizarin red, and rinsed
21. rinsed with water, treated with blind vat, and rinsed
22. idem, dyed with Anthrasol O, and rinsed

1) soap consisting of almost pure sodium-oleate. This soap satisfies the requirements of British Standard BS 1912 : 1953

All these differently treated yarns were then exposed to one or more of the 15 different ageing methods. In paragraph 3. of this report the exposure of one material to one ageing method will be called a series of experiments.

3.2. Methods of testing

a. Determination of the breaking load and

b. Determination of the elongation at break of the yarns at gauge length of 500 mm

c. Analysis of amino acid content

  1. cystine ("SS+SH") (inter- and intramolecular cross-linking amino acid), by a polarographic method on the intact fibre according to Leach
  2. cysteïc acid ("$CySO_3H$") (end-product of the degradation of cystine), by an electrophoretic method after hydrolysis.

3.3. Discussion of the results

3.3.1. General

As in the case of cellulose yarns we were unable to assess an unambiguous coefficient of degradation for each ageing method investigated. Nevertheless we developed a rather rough method to appraise the severeness of degradation.

This method is briefly discussed below.

Since the materials were aged over different periods of time it was possible to draw diagrams of a certain property y (e.g. breaking load) versus time t. In all cases the experimental data could be fitted rather well into an algebraïc formula of the general form $y = A + B.e^{-k.t}$.

In this formula A and k are variable parameters, and B has the value $B = y_o - A$ (y_o = value of the property under consideration at time zero, that is the value of y of unaged material). In figure 3.1 some curves are drawn with varying values of A (k being kept constant), and with varying values of k (A being kept constant). From this figure it can be seen that the value of k is an indication of the rate of decay of the property, whereas A is an indication of the value of y at infinite time.

In principle it should be possible to calculate A and k from the experimental data of each series of experiments. Actually we were

unable to calculate A and k for several properties in many series, especially for the breaking load. This was mostly due to irrelarities in the experimental data. However, by choosing a fixed value of A for all series we were able to calculate k. The choice of the fixed value of A was based on information from measurements made on very old materials, of which it could be assumed that y had nearly reached the true value of A.
(This aspect will be discussed extensively in the final report on this researchproject, to be published)
With the chosen, c.q. calculated values of A, and the calculated values of k for each series a curve could be constructed. In most cases these curves matched the experimental data reasonably well. Two examples are given in the figures 3.2 and 3,3.
Now the values of A and k for all four measured properties (mentioned in 3.2) in each series were transformed (in a rather arbitrary way, the merits of which will be discussed in the final report, to be published) into one overall so-called "rate of degradation" (r.o.d.), which made possible the comparison of the series with each other. We are aware of the fact, that this "r.o.d." is by no means an exact representation of the degradation, but nevertheless it is useful in appraising the influence on the degradation of ageing methods and treatments of the wool.
It must be stressed here, that strictly speaking conclusions will only be valid for the materials and methods of ageing investigated, as too much generalization may lead to erroneous conclusions, because we found that, as with cotton, the rate of degradation is also dependent on the previous history of the materials. Bearing this in mind our experiments have led us to the following conclusions.

3.3.2. Experiments in the absence of light

a. At the high relative humidity (r.h.) (90 % r.h.) the rate of degradation (r.o.d.) is much higher than at the low r.h.(10 % r.h.).
b. Wool washed with soaps or detergents degrades somewhat faster than wool only rinsed with water. The "natural" anionic soaps caused a little less degradation than the synthetic anionic and nonionic detergents, especially Nekanil O extra at low r.h. gave a rather high r.o.d. The domestic detergent, containing

bleaching agent and optical brightener, caused heavy damage, both at low and at high r.h.

c. Wool extracted with di-ethyl-ether showed rather heavy damage, especially at high r.h.

d. In the dark wool dyed with chrome mordant dyes degrades somewhat faster than undyed wool, and relatively even faster at the lower r.h. ; the fustic and alizarin dyed wool showed the highest r.o.d. The vat dye Anthrasol O (indigo) showed about the same r.o.d. as fustic and alizarin. The other dyes showed little differences between each other.

e. The behaviour of acid treated wool on degradation is dependent on the type of acid used. Formic acid and acetic acid treatments seem to protect wool against degradation in the dark. The r.o.d. of the so treated wools is less than the r.o.d. of wool rinsed with water, irrespective of the pH-value, especially at the low r.h. Sulphuric acid treated wool, however, shows a different behaviour. At the lower r.h. only at a pH-value of 5.0 there is a decrease in r.o.d. as compared to wool rinsed with water, at pH-values of 3.5 and 2.0 the r.o.d. is about equal to that of wool rinsed with water. At the high r.h. the sulphuric acid treated wool degrades much faster than wool rinsed with water, especially at a pH-value of 2.0. There were also indications that the previous history of the wool has an influence on the behaviour of this wool when treated with sulphuric acid. The conclusion must be, that, if for any reason an acid treatment is necessary, sulphuric acid should be avoided, but one should rather use formic acid or acetic acid.

f. In the dark the influence of air pollutants (sulphur dioxide SO_2, nitrous oxides NO_x, and ozone O_3) on wool rinsed with water was examined. All these gases caused a considerable increase in the r.o.d. of the wool as compared to wool aged in the same way in purified ambient air. SO_2 and NO_x are the most harmful gases, separately as well as in combination. Ozone seemed to be less detrimental in its effect on the r.o.d., the r.o.d. of wool aged by ozone being only slightly higher than the r.o.d. of wool aged in purified air. However this result may be due to the low concentration of ozone used, as compared to the concentrations of SO_2 and NO_x used.

3.3.3. Experiments in the presence of light

a. The r.o.d. is highly increased by irradiation with light, the value of k being increased by a factor 10 to 100 as compared to identical experiments in the dark.

b. Soaps and detergents only slightly increase the r.o.d. as compared to wool rinsed with water.

c. Wool dyed with the investigated chrome mordant dyes is more resistant to light degradation than undyed wool. There are, however, differences between the different dyes. Fustic and logwoog show a greater ability of protection as brasil wood and alizarin. This phenomenon might be explained by the light-absorbing properties of the dyes.

d. SO_2 and NO_x, separately as well as in combination, caused heavy damage, as is the case in the dark, but now at a much higher level. The experiments with ozone showed much less degradation of the wool, again probably due to the relatively low ozone concentrations used.

4. DENSITY, MOISTURE SORPTION AND SWELLING IN WATER OF HIGHLY DEGRADED NATURAL FIBRES

Summary of results.

1. Degradation by light of wool, linen and cotton involves a slight decrease of the capacity of these fibres to absorb water from an atmosphere with a relative humidity of ca. 60 %. This r.h. lies in the region of the sorption isotherm where the water molecules are bound to chemically active sites, e.g. by hydrogen bonding.
2. Likewise a tendency could be observed (by density measurements) that the fibres attain a denser structure.

   Both phenomena are most pronounced in wool, especially in the case of wool aged by light in a very dry atmosphere (r.h. < 0.05%), and the least in the case of bleached cotton.
3. Unexpectedly it was observed that part of the degraded wool material became soluble in water. In the case of wool degraded in a very dry atmosphere ca. 16.5 % by weight dissolved in water.
4. In an atmosphere of 99 % r.h. highly degraded wool is able to absorb water in higher percentages than undegraded wool.

   This fact might be explained by the phenomenon mentioned under 3.

In the case of highly degraded raw cotton a similar increased water sorption capacity was observed in this very humid atmosphere. Further investigations in this field are still in progress.

5. Tests carried out on a highly degraded tightly woven cotton fabric showed that repeated swelling of the fibres, brought about by immersion in water followed by drying, did not cause any appreciable additional weakening of the fabric. Similar tests on a wool fabric are in progress.

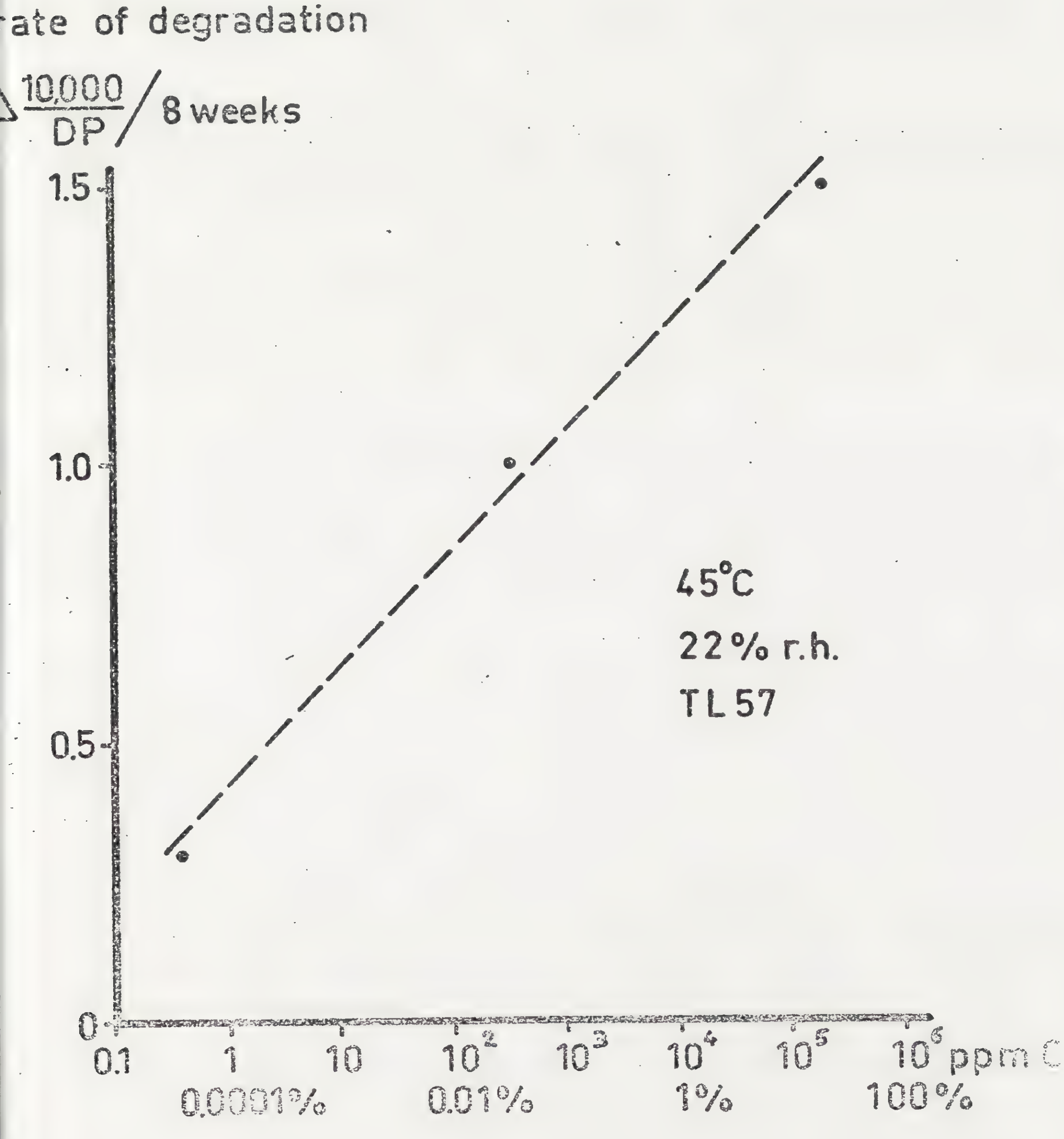
5. CONCLUSIONS AND RECOMMENDATIONS

1. The rate of degradation of a textile material, wholly or partly consisting of cotton, linen and/or wool, is hardly predictable, even when the ageing factors of the environment are known.
2. To retard degradation certain precautions may be taken :
   - a. Exclusion of light as far as possible, also of ultraviolet and of infrared light, because the degrading effect of irradiation is much larger than the effects of any of the other degrading factors. The exclusion of light is the most important weapon against degradation of textile materials.
   - b. Removal of pollutants from the atmosphere.
   - c. Avoidance of higher temperatures, originating from light incidence, central heating, sunshine, etc.
   - d. Avoidance both of extremely low and of high relative humidities.
   - e. Reduction of the oxygen concentration in the surrounding atmosphere to the level of a few hundred parts per million or less.
   - f. Avoidance of material stresses.
3. When an investigation is made on the influence of any degrading factor as such (e.g. air pollutants, temperature, humidity or chemical agents), the experiments should be made in the dark. This is because the degrading power of light is so large, that it is apt to overshadow the effects of the degrading factor under investigation.
4. By degradation the water sorption isotherm of textile materials changes its character.
5. Highly degraded wool proved to be partly dissolvable in water. Consequently one has to be very cautious in washing decayed wool materials.

6. REFERENCES

1. J.E.Leene, Artificial ageing of yarns in presence as well as in absence of light and under different atmospheric conditions, Interim Report, ICOM, Washington, 1965
2. idem, Second Interim Report, ICOM, Brussels, 1967
3. idem, Third Interim Report, ICOM, Amsterdam, 1969
4. R.J.Elema, A.H.J.Nijhof, A model for the degradation of cotton cellulose, J.Polymer Sci. C, to be published.

The influence of oxygen.



Rate of degradation vs. O_2-content at irradiatio

The interaction of degrading components and factors.
(8 weeks irradiated, TL 57, 45°C, 22% r.h.)

material	pollutants	g.s.			
		a	b	a + b	c
raw cotton	SO_2	1.5	0.6	2.1	5.6
" "	NO_2	1.5	0.9	2.4	8.8
" "	SO_2+ NO_2	1.5	1.4	2.9	3.4
" "	O_3	1.5			
bl.cotton	SO_2	1.2	0.8	2.0	12.0
" "	NO_2	1.2	0.6	1.8	4.8
" "	SO_2 + NO_2	1.2	5.0	6.2	14.4
" "	O_3	1.2			
linen	SO_2	1.4	0.6	2.0	4.3
"	NO_2	1.4	0.4	1.8	3.6
"	SO_2 + NO_2	1.4	0.8	2.2	5.4
"	O_3	1.4			

a. irradiation in an unpolluted atmosphere.
b. polluted atmosphere, no irradiation.
c. irradiation in a polluted atmosphere.

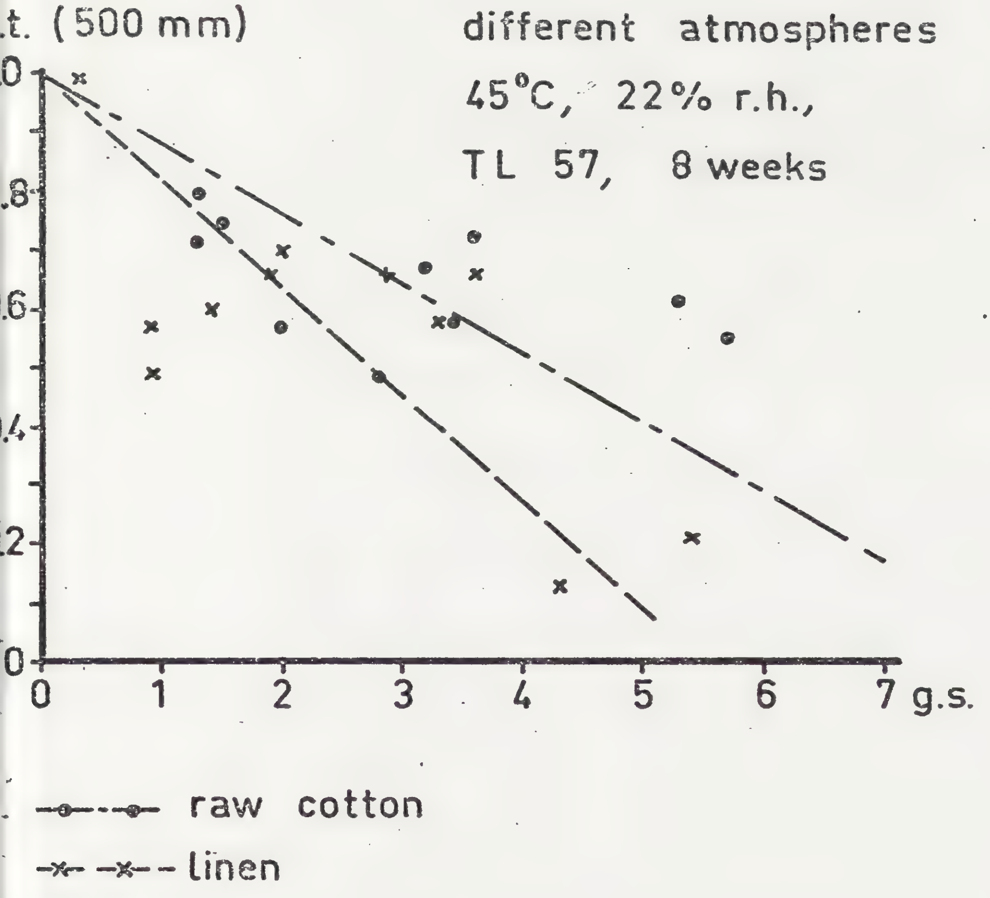
Table 2.1

The influence of spectral energy distribution.
(8 weeks irradiated, 40°C, 22% r.h.)

Lamp	g.s.		r.t. (500 mm)	
	raw cotton	bl.cotton	raw cotton	bl.cotton
TL 40/8	-	5	-	0.61
TL 40/57	2	3	0.74	0.85
TL 40/34	1	2	-	-
TL 40/37	0	1	0.95	0.90

Table 2.2

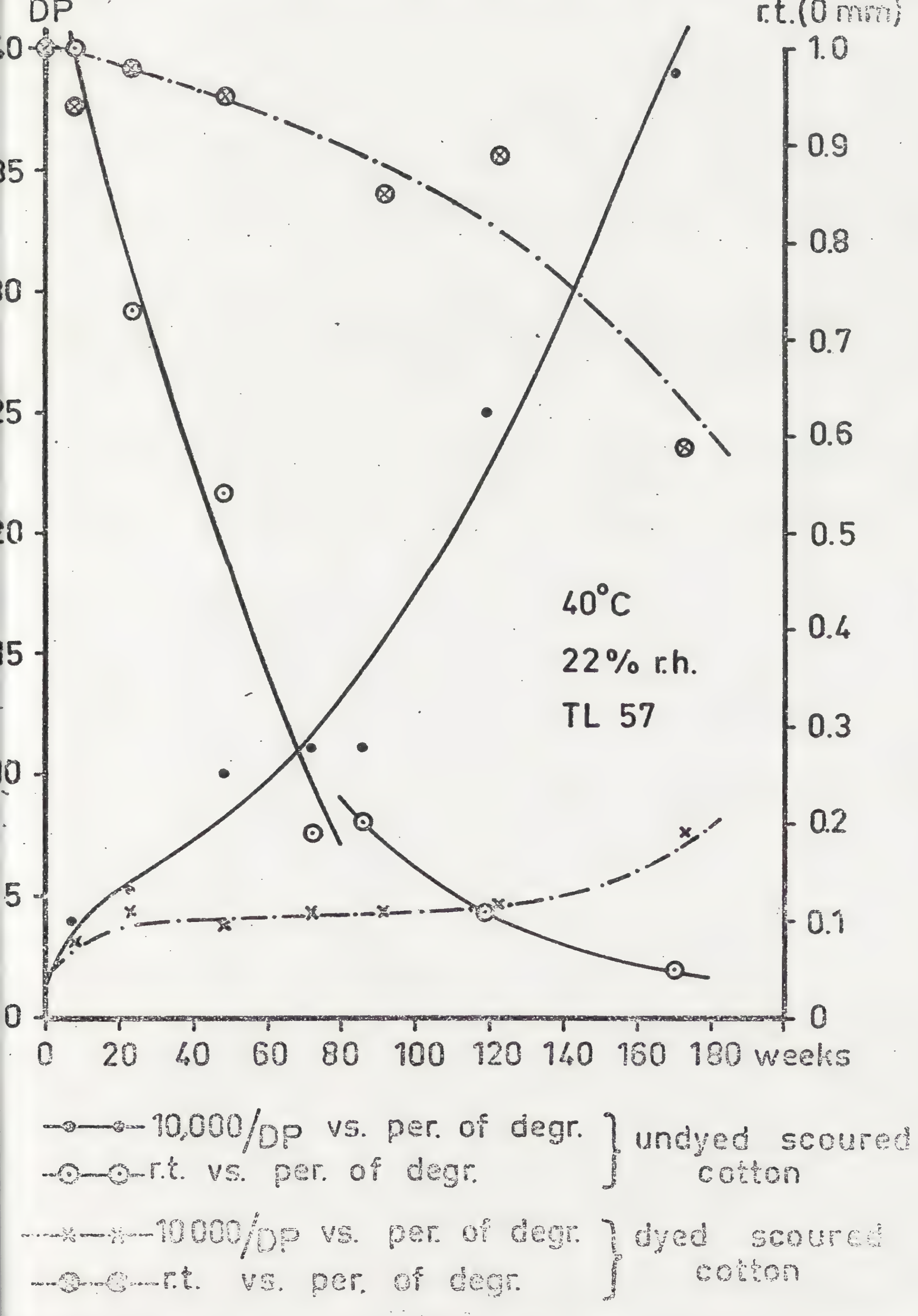
ifference in behaviour of cotton and linen.



Relative tenacity vs. grade of scission.

Figure 2.2

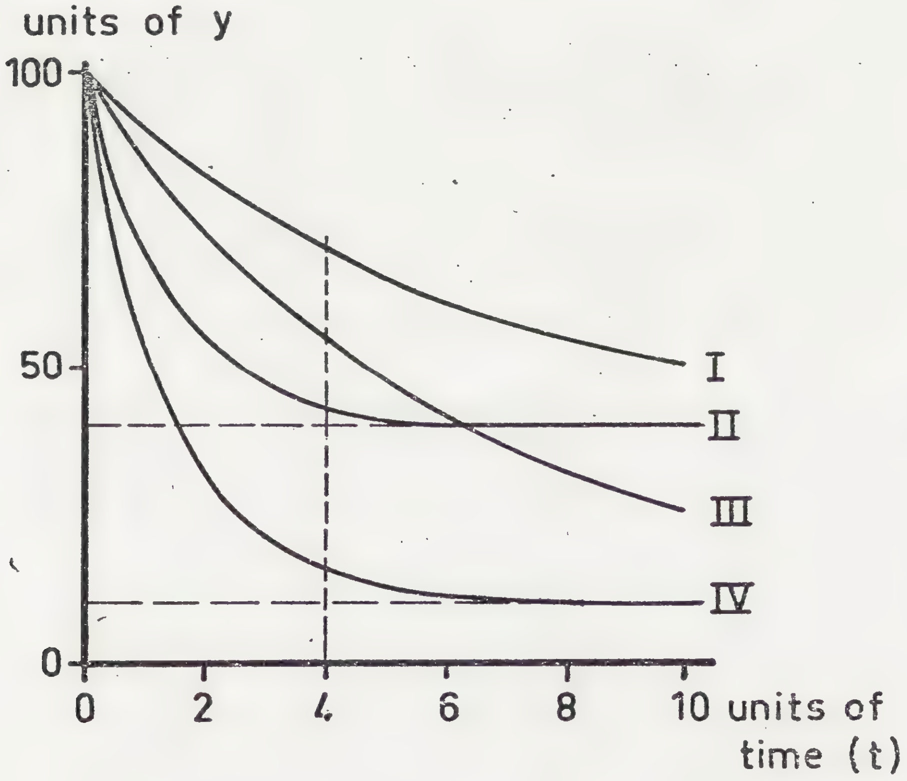
The influence of mineral khaki.



Graphical representation of the curve.

$$y = A + Be^{-kt}$$

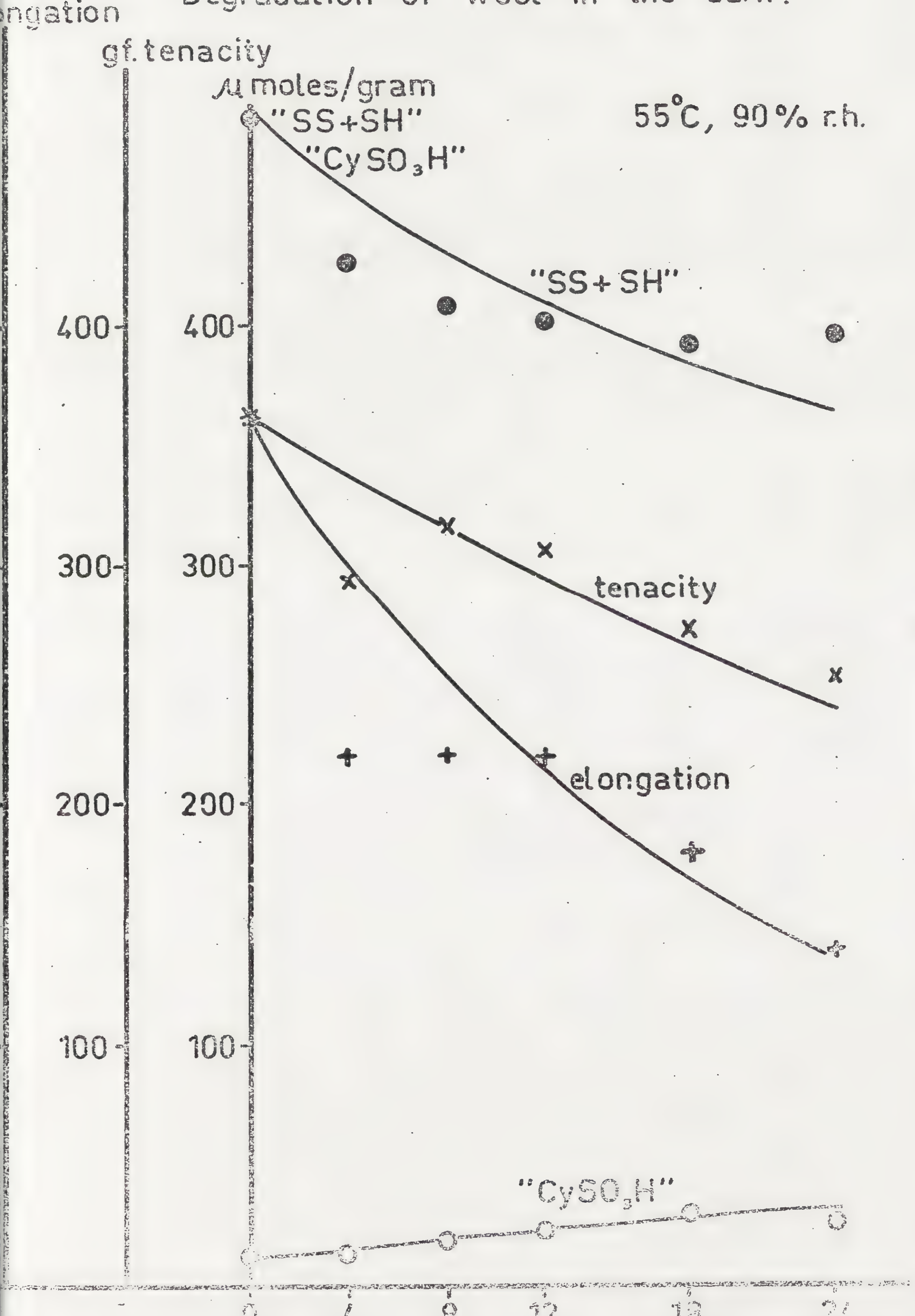
at differing values of A, resp. k.



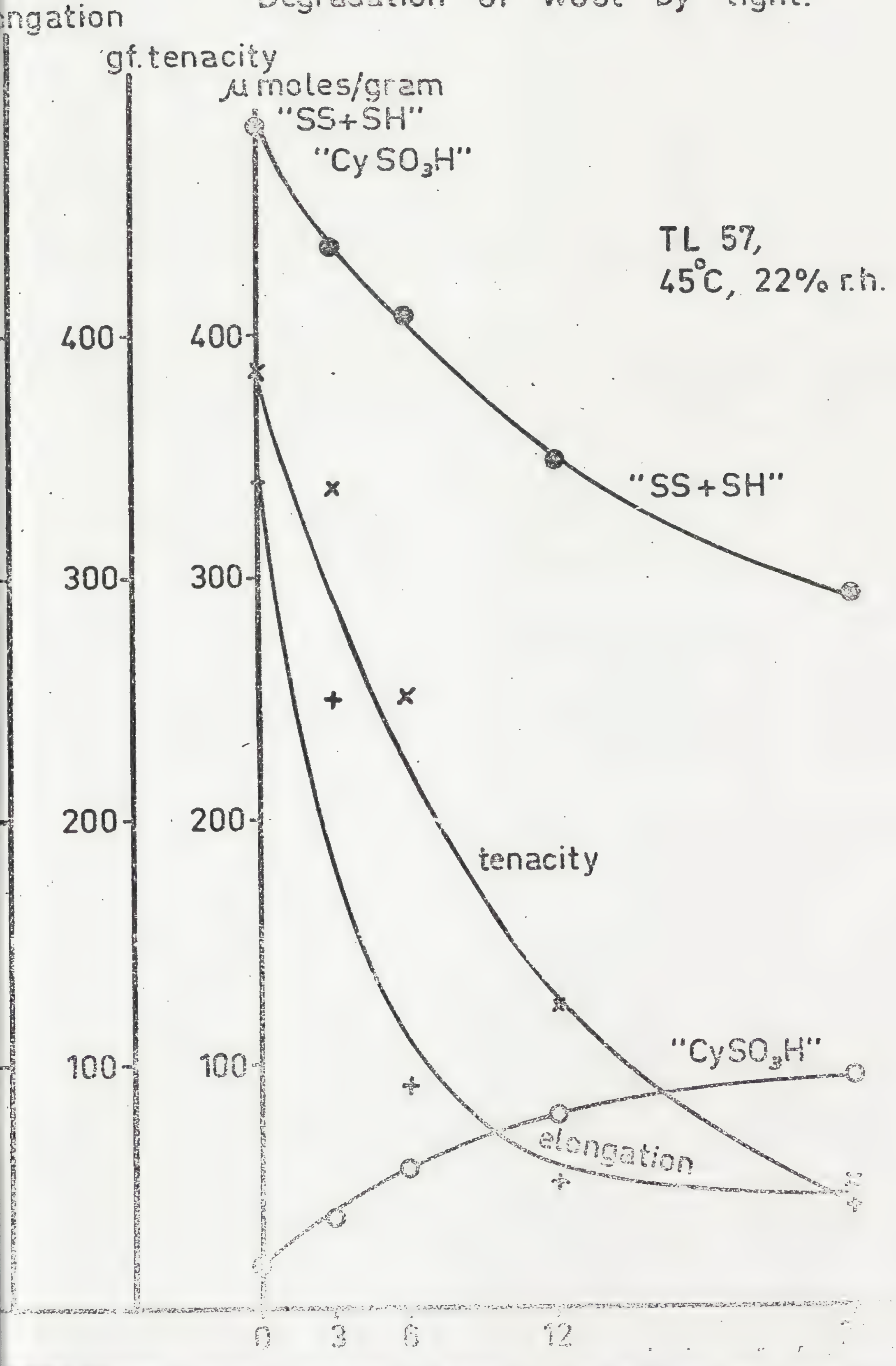
curve	A	k
I	40	0,175
II	40	0,639
III	10	0,175
IV	10	0,639

Figure 3.1

Degradation of wool in the dark.



Degradation of wool by light.



ABEGG-STIFTUNG BERN

TEXTIL-ABTEILUNG CH 3132 - RIGGISBERG (BERN)

The Care of Historic Fabrics illustrated by the Grave Garments of Sigismondo Pandolfo Malatesta

by Mechthild Flury-Lemberg

As we have to do in preserving every work of art our aim must be to hand an historic textile down to the future in as authentic a condition as possible. We must be guided in this by the present condition of the material, however fragmentary it may be. The work of conservation cannot therefore proceed until the piece has first been scientifically classified. Then it has to be decided whether later additions should be removed, if they are of no historic value.

Repairs done in the past may afford clues to the history of the piece, so careful consideration has to be given as to whether they should be retained as historical evidence. Also, it is essential to keep a written record of all the observations made on the fabric and of everything done to preserve it. The choice of method is determined by the need for it to be reversible. Anyone who has had to free works of art from the stranglehold of previous restorations after time had shown that certain methods, however well meant, were inadmissible, will realize that every conservation treatment must be reversible without damage to the material. Of course, the restorer works to the best of his ability and in good faith, hoping that the results will be acceptable in the distant future. Yet, now more than ever before, we see how short-lived certain methods may be. We must not assume that we have ever found the ultimate solution to the problem; the door must always be left open for a better method of treatment. These basic rules, which hold good for any work of conservation, apply equally to the treatment of textiles.

When the precious materials come into our hands they are twice

with dust and foreign matter which has often become lodged in their fibres in the course of centuries. Old fibre is naturally more fragile than new and is more likely to be damaged by any additional strain. Thus the first and most important step in conservation is to remove these impurities, which are an irritant to the fibres, often embed them completely and deprive them of what remains of their elasticity. Needless to say, great care is required and the object must be handled as gently as possible. What has to be borne in mind is not only the immediately deleterious effect which the treatment may have, but also the possibility of detrimental action which will not become apparent until years later. This applies in particular to cleaning materials which leave in the material residues whose long-term effects are not known.

It is important, therefore, to employ a well-tried method. Water is a good example. As far back as our knowledge goes, textiles have been cleaned in water. It may be supposed that all the pieces preserved for us came into contact with water at the time they were made and suffered no damage. In addition water has properties which are beneficial to these old and often matted and crumpled fabrics. Only with the aid of water can the fibres be straightened and harmful creases eased out of the material. The addition of a minimal amount of a neutral washing agent helps to dislodge dirt without attacking the actual substance of fibres. Particles of dirt loosened in this way can then be removed without mechanical methods. It is often sufficient to agitate the piece gently in the washing water, and then rinse it several times to shift the foreign matter along with the remaining washing agent. The wet fabric is straightened out and when it has dried a perfectly smooth surface is obtained without the heat and pressure of ironing.

This first conservation treatment is highly important, because it eliminates the harmful influences to which the material was previously exposed. After removal of the dirt the fibre is reactivated and can breathe again. If the fabric has no brittle places this treatment may suffice in itself; otherwise it must be reinforced.

In this context attention must be drawn to the possible consequences of using chemical methods of conservation which have not yet been adequately tested. It cannot be denied that the current experiments in chemical textile conservation hold out favourable prospects for the treatment of certain pieces. However, they cannot be expected to be passed as fit for use for a long time yet because, as has been explained, years of observation are necessary for full understanding of their effects on brittle fabrics. Only when their harmlessness has been proved shall we venture to treat our precious ancient textiles with these agents. Until then preference will be given to methods whose reliability is vouched for by time and experience, and which, unlike the chemical techniques known to date, can be reversed without damage to the ancient fabric.

One of the methods which is reversible at any time without danger to the fabric is reinforcement by mounting on cotton, linen or silk fabric, using very fine silk thread and correspondingly fine needles Flaws in the old material can be concealed by colouring the backing fabric to compensate optically for the colour difference and so restore to the fabric throughout its original appearance. (It is important to use dyes of the very highest light fastness). The delicate overcast stitches of dyed silk thread can as a rule be seen only on careful inspection and, because of their fineness, they place no strain on the fabric. Silk hair threads are particularly suitable for this purpose because they have just the degree of durability required. Nylon thread, which is much thicker and more durable, would cause damage precesely because of its strength. Owing to its limited elasticity and the marked discrepancy between it and the fibre it is entended to protect, the stitches cut the brittle fabric and ultimately only the nylon thread survives. The same is true of man-made fibre fabrics; as backing, these have too little elasticity and, although sometimes very fine, they are too rigid for our textiles. The durability of a new fabric of cotton, linen or silk (provided it is used without finishing) makes it just right as a backing since it is naturally greater than that of the centuries-old textiles. it serves to protect.

These are the principles to be observed in caring for works of textile art. Each single item is looked upon as a patient who has to be treated according to his individual characteristics as it now

shall be exemplified by the conservation of the grave garments of Sigismondo Pandolfo Malatesta. The example is chosen to contradict a modern technical opinion of textile conservation saying the only possibility to preserve old fabrics in a bad condition is the heat-sealing or glueing method. The material of the present garment could not be in a worse state, but we did not follow the modern trend and its simplifications, there are no single ways in our methods. The restoration method has to be individual and has to respect the condition of the single object. We tried to find out not one but several proceedings - excepted the glueing method - which we considered suitable to the special conditions of the textile rests, and I am now going to show you the results.

The Conservation of the Grave-Garments of Sigismondo Pandolfo Malatesta

The old Gothic church of Rimini, dedicated to St. Francis, was also the family burying place of the Malatesta, the local dynasty of Rimini. Sigismondo Pandolfo Malatesta, who lived from 1417 - 1468, transformed it after 1442 into one of the outstanding monuments of the early Renaissance in Italy. The great Leon Battista Alberti himself re-designed the principal facade in the style of a Roman triumphal arch, after the Augustan arch of Rimini. The reconstruction of the Gothic interior of the church was not finished: only the three first side chapels on each side are re-built in Renaissance style. They contain masterpieces of sculpture by Duccio and the famous fresco by Piero della Francesca. The fresco by Piero della Francesca shows Sigismondo Pandolfo Malatesta kneeling before the tutelary saint, Sigismond of Burgondy.

This portrait of Malatesta gives an idea of the person who was buried in the clothes we are interested in. He lives in history as a gifted man, devoted to culture and art, but full of criminal instincts, Pope Pius II (better known under the name of Aeneas Silvius Piccolomini), who excommunicated him, said of him : "He was born to everything he did, even to the most wicked and atrocious."

His sculptured stone coffin was first opened on the 31st August 1756, 288 years after his burial.

We have the record of the opening and a drawing by Giovanni Antonio Battara showing the site and the state of the contents. As the drawing shows, the parts of the garments were still intact at this date, except for the stockings and shoes. The decay must have taken place later on.

The second opening took place on the 28th of September, 1920, 452 years after the burial. The record of A. Tosi says: "The clothes of Sigismondo were fallen to pieces so small and crumbled that in spite of the well-known skill of signora [illegible] it was impossible to make even a partial reconstruction". According to the same report the crumbled pieces were collected in appropriate boxes, and typical specimens of each garment were put under glass for display. So [illegible] of the grave-clothes of Sigismondo which it was possible to display

have been exhibited since the second opening of the tomb in the reliquary chapel of the Malatestian temple.

Other fragments were crammed for 50 years into a small wooden box, as you see here. We received this box at the Abegg-Foundation in Spring 1970, measuring 34 cm long, 25 cm broad and 12 high, together with three glass frames containing the larger fragments.

The latter fragments were five pieces of brocaded silk each measuring about 20 to 40 cm, they are the rest of Sigismondo's cloak.

We sorted the contents of the wooden chest which consisted of very small pieces of all the garments. We found innumerable fragments of the brocaded silk, bits of the brocaded velvet of which the jupon was made, fragments of the linen winding-sheet sticking together in a hard lump, and remains of a very interesting tablet weave, which must have served as a girdle.

We started the conservation with the brocaded silk, the material of Malatesta's cloak. You see the small fragments of the brocade before washing, and after washing, laying out and drying. It will easily be seen that the pieces were in too fragmentary a state to allow a conclusion to be made about the exact nature garment. In particular, we could not find any pattern relating to the garment worn by Sigismondo in Piero della Francesca's painting or in the drawing made at the time of the first opening of the tomb.

Therefore the only intention of the conservation was to find the pattern of the piece.

We took the bigger fragments of the brocaded silk and made a drawing which reconstructed the pattern unit. Since many selvage-fragments remained, making up a whole or a half rose of the pomegranate motif, which were brocaded with gilded silver threads on a diaper satin ground, it could be seen that one and a half roses of the pomegranate made together the usual medieval measurement of 55 cm for the width of a piece.

We made blue-prints of our drawing and put a few pattern units together. Then we distributed all the fragments according to their pattern on these blue-prints, taking great care not to

In this way we reconstructed a length of the brocade of 2,24 meters and were able to read the pattern without difficulty. Considering the fragile state of the fragments, we decided to keep them under glass. We transferred piece after piece from the drawing on to felt, dyed in the actual brown tone of the brocade. Over the fragments we placed a piece of brown silk crepeline, which we fixed with a few stitches, so that the glass can be taken off without disturbing the order of the fragments found with much patience and difficulty.

You see the prepared piece on a wooden mount before being covered with glass. The mount was also overlaid with felt to give the fragile fragments a soft base.

The fragments of the brocaded velvet were all together in the wooden chest. We saw small and very tiny pieces, dirty, broken, crumbled, rolled up, mixed with the dust of completely decayed fragments. Only traces of pile and the metal threads of the pattern were to be found.

When sorting the fragments we were struck by pieces showing extraordinary features:

You see the front fastening showing buttons and buttonholes and the sewed slope of the neck, lined with linen quilted in straight lines.

Fragments of the front fastening with buttonholes without any marks of quilting.

The waist-seam with quilted and unquilted parts, and fragments with gathered edges.

You see fragments lined with linen quilted in round lines, and the reverse of a fragment, where you can see the linen lining quilted.

And, lastly, fragments with a seam and rings.

Because of the fragile state of these fragments, we did not wash them but only soaked them in water. All the pieces described must have been parts of a garment. The report of the second opening of the tomb gives an exact description of the garment Sigismondo wore under the brocaded cloak:

It was a jupon or doublet with sleeves reaching down to the groin, narrow in the waist, made of velvet "tagliato con sopra-riccio d'oro", with small rings on both sides, and with small

With the help of this description we were able to reconstruct the characteristic parts in such a way as to show the whole structure of the garment. We had the line of the neck slope, the front-fastening with button and buttonholes, and some fragments of them with distinct remains of quilting, which we placed at the upper part of the jupon in the way in which we know that these garments were made. Others, without any traces of quilting, we placed at the lower part; also the waistseam showed one quilted and one unquilted side and the state of the buttonhole clearly showed that the lower part of the garment must have been unquilted. We had some fragments of the armholes but it was difficult to place the parts with gathered edges and the fragments with the rings, of which the report says: they were on both sides.

But we had the luck to find a Florentine costume-drawing of the same date. It shows a man in under-garments wearing a doublet or jupon corresponding exactly to the description of the opening record. It was a jupon with sleeves reaching down to the groin, narrow in the waist, and with small rings on both sides, with small buttons fixed on the right side. So we concluded that the gathered fragments were parts of puffed sleeves and the fragments with the rings were to be placed on the lowest end of the garment, just over the thighs, where they must have served to fix the hose on the jupon. So our jupon-puzzle was solved and all because of the costume-drawing.

Having no clues concerning the measurements of the jupon we had to be satisfied with a schematic reconstruction, and conserved the plain fragments of the brocaded velvet separately. The reconstructed garment was sewn between two sheets of silk-crepeline.

You will see that the conservation of the jupon was a different matter from the length of brocade. Out of the latter we were able to make a sort of display piece which was impossible with the not only small, but ugly and discoloured fragments of the jupon. But the result is, all the same, a very satisfying proof of the historical identity of the garment and a contribution to the history of costume.

At the bottom of the wooden chest we found two fragments of the linen winding cloth, hardened by dirt and humidity into hard lups. We soaked them in distilled water during two days and two nights. The detached fragments were washed, laid out and dried. We found nondescript fragments, others showed a selvage and others again a seam, and we concluded that two straight pieces had been sewn together. So we see a certain probability that the fabric has been used as a winding sheet. We mounted these pieces together between two sheets of crepeline.

We further found in the box five other linen fragments in a completely rusted and hardened state. Three of them were treated with an anti-rust agent, the two others were left in their original state for documentation. We presume that these rusted parts of the winding sheet must have been near the iron weapons.

Last of all, the wooden box contained ten pieces of a band of tablet weaving. Three pieces show the widths of the band, which is 4 cm. All these fragments were very rusted, partially hard and fragile. We consider the band to be the most interesting fabric of all. It is not only decorated with looped gold thread but also with pile and fringes. It must have served as a girdle, corresponding to the description of the first opening.
To eliminate the rust marks from the girdle, we used a solution of Kaliumbifluorid and after this treatment we washed and dried the fragments as usual. We wanted to conserve this very interesting piece in a way that would not cover the reverse permanently, so we sewed it between two sheets of crepeline, put it on a wooden mount overlaid with a silk fabric, framed it with a thick passepartout and covered it with glass. Glass and passepartout are easy to detach so that the reverse can be studied.

In conclusion, I should like to thank my staff, and particularly Brigitta Schmedding, for having done the conservation work.

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FLEXIBILITY OF FABRICS

III

AGEING OF ADHESIVES, USED IN TEXTILE CONSERVATION

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Flexibility of fabrics

III

Ageing of adhesives, used in textile conservation.

In this paper the results of ageing experiments on several adhesives used in textile conservation are discussed.

1. Adhesives.

Polyvinylbutyral: Mowital B 60 HH

Polyvinylacetates:

- Mixture of Mowilith DM5 and Mowilith DMV 1 (equal parts)
- Mixture of Mowilith DM5 and Mowilith DMC 2 (equal parts)
- Mixture of Mowilith DM5, Mowilith DMV 1 and water (equal parts)
- Mixture of Mowilith DM5, Mowilith DMV 1 and Vinamul N 6525 (equal parts)
- Mixture of Mowilith DM5, Mowilith DMV 1, Vinamul N 6525 and water (1:1:1:2)
- Mowilith VP 555 and water (2:4.6)
- Mowilith VP 555 and water (2:1.5)

Acrylic resin:

- Paraloid F-10

2. Method of application on the test fabrics.

   1. Impregnation (Mowital B 60 HH)
   2. Coating (the other adhesives)

3. Ageing methods.

   1. No light, 20 ± 1°C, relative humidity 65 ± 2 %.
   2. Temperature, relative humidity as well as intensity of light not constant. Box, covered with a glass lid, was exposed to daylight near a window looking to the south, and to the ambient air of a non-conditioned room.
   3. No light, climate cabinet, 40° C, 80 % r.h.
   4. No light, climate cabinet, 40° C, 15 % r.h.

4. Testing method.

The flexibility has been measured according to the cantilever method, developed by Peirce (Journal of the Textile Institute, 21(1930) T 377.

Measured were:

1. Bending length, which is according to ASTM - Designation D 1388 - 64 - "a measure of the interaction between fabric weight and fabric stiffness as shown by the way in which a fabric bends under its own weight. It reflects the stiffness of a fabric when bent in one plane under the force of gravity, and is one component of drape". The definition in BS 3356 : 1961 states that it is " one of the factors that determine the manner in which a fabric drapes. It is related to the quality stiffness that is appreciated by visual examination of the draped material, in the sense that cloths having a high bending length tend to drape stiffly."
2. Flexural rigidity, which is according to the ASTM - Designation D 1388 - 64 "resistance to bending". In BS 3356 : 1961 it is defined as "a quantity which is a measure of the resistance of the cloth to bending by external forces. It is related to the quality stiffness that is appreciated when a fabric is handled, in the sense that cloth having a high flexural rigidity tends to feel stiff."
   It is calculated from the weight q (mg/cm^2) and the bending length c (cm), according to the formula:

   $$G \text{ (flexural rigidity)} = q\,c^3 \text{ mg cm.}$$

   The measurements were always made on the same strips to exclude the variability in the fabric itself and in the distribution of the quantity of adhesives over the surface of the treated fabric.

5. Discussion of the results.

The strips coated with Paraloid F-10 or with polyvinylacetate adhesives (Mowilith, Vinamul) show during measuring a different behaviour from those of untreated fabrics and of the Mowital samples.
The closed films of Paraloid as well as of Mowilith have a retarding effect on the bending of the strips. With fabrics normally the bending is nearly independent of time, and therefore it is more or less correlated with drape. But in the case of Paraloid as well as of Mowilith treatments, especially for the larger applied quantities of these adhesives, there is a distinct dependence on time. Therefore it was necessary to measure after an arbitrarily chosen time of 30 seconds. This means that the drape is distinctly impaired by the application of these coatings.

re has been no opportunity for further investigation of this phenomenon.

e ageing properties of Mowital B 60 HH are excellent. The samples after x years of ageing by method 3.1. as well as the samples aged by method 2. showed no change in flexural rigidity (tables 1 and 2).

the whole the ageing properties of the different types of Mowilith under e conditions of method 3.2. have also been very satisfactorily (table 3). t the acrylic resin Paraloid F-10 got a distinctly higher flexural gidity (table 4).

e behaviour of the coatings at a higher temperature and at different midities has been investigated in climate cabinets (methods 3.3. and 3.4).

general it was found that the Mowilith - coatings maintained the same vel of flexural rigidity, with the exception of Mowilith VP 555 which owed a significant increase. But a large disadvantage of all these coatings s that they got sticky at the higher temperature. This stickness could ove to be an inacceptable property, when these adhesives should be applied objects which must be kept in tropical climates.

e investigated Paraloid - coating stiffened very distinctly under the dif- rent test conditions, but it showed no stickiness under the conditions in e climate cabinets.

could be of interest to investigate systematically the behaviour of the fferent adhesives in hot, dry atmospheres as well as in hot, humid atmos- eres when applied in the same way as on a restored object, where the ating is the connecting layer between object and supporting fabric.

all our experiments it has been found that the behaviour of the adhesives the long run is predictable after an ageing test of 16 weeks.

geing of Mowital B 60 HH, no light, 20± 1° C, 65 ± 2 % r.h.

abric	%-age Mowital	Weight (mg/cm^2)		Bending length (cm)		Flexural rigidity (mg/cm)	
		October 1966	July 1972	October 1966	July 1972	October 1966	July 1972
otton	0	12.05	-	2.2	-	129	-
plain	0.01	12.74	12.29	2.2	2.0	139	103
weave)	0.05	12.63	12.46	2.2	2.1	144	109
	0.10	12.15	12.92	2.2	2.2	152	130
	0.50	12.75	13.00	2.2	2.2	174	142
olyester	0	2.90	-	1.7	-	14	-
ousseline	0.01	2.90	2.81	1.7	1.8	15	17
	0.05	2.91	2.82	1.7	1.8	15	16
	0.10	2.93	2.90	1.8	1.8	18	17
	0.50	2.90	2.86	1.9	1.8	19	17
ilk	0	0.75	-	3.2	-	25	-
repeline	0.01	0.79	0.75	3.3	3.3	29	26
	0.05	0.70	0.76	3.3	3.4	26	29
	0.10	0.78	0.76	3.4	3.5	30	32
	0.50	0.80	0.72	3.4	3.4	32	27

Table 1.

Ageing of Mowital B 60 HH on polyester crepeline fabric.
(Temperature, relative humidity and light not constant)

Percentage adhesive	Weight (mg/cm^2)		Bending length (cm)		Flexural rigidity (mg x cm)	
	July 1969	June 1972	July 1969	June 1972	July 1969	June 1972
0	1.41	–	1.6	–	6	–
0.01	1.42	1.38	1.7	1.7	7	6
0.05	1.44	1.40	1.7	1.7	7	8
0.10	1.44	1.41	1.7	1.7	8	8

Table 2.

Ageing of mixture of Mowilith DM 5 and Mowilith DM V 1 (1:1) on polyester fabric.
(Temperature, relative humidity and light not constant)

Quantity of adhesive g/m^2	Weight (mg/cm^2)		Bending length (cm)		Flexural rigidity (mg x cm)	
	July 1969	June 1972	July 1969	June 1972	July 1969	June 1972
0	1.34	–	2.2	–	15	–
11.22	1.93	1.94	2.2	2.4	22	26
22.44	2.91	2.92	2.0	2.0	22	26
33.66	3.90	3.93	1.8	1.8	23	26
44.88	5.16	5.18	1.6	1.7	22	25

Table 3.

geing of Paraloid F-10 on polyester fabric
temperature, relative humidity and light not constant)

uantity of dhesives g/m^2)	Weight (mg/cm^2)		Bending length (cm)		Flexural rigidity (mg x cm)	
	July 1969	June 1972	July 1969	June 1972	July 1969	June 1972
0	1.34	–	2.2	–	15	–
11.22	1.72	1.73	2.7	3.2	33	55
22.44	2.88	2.90	2.7	3.1	55	84
33.66	4.34	4.38	2.5	2.9	67	110
44.88	5.61	5.40	2.2	2.8	61	115

Table 4.

groupe 12/13

National Museum of Canada

National Museum of Man

Ethnology Division

CONSOLIDATION OF PAINTED WOODEN ARTIFACTS

by

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ABSTRACT

Problems of consolidation by monomer impregnation are discussed in general and three case histories of restoration of painted artifacts described. Polymerization reaction of the methylmethacrylate monomer was initiated by either gamma radiation or 4-t-butylcyclohexyl peroxidicarbonate with pyridine as activator at slightly elevated temperature (45°C). In order to avoid excessive warming during the reaction the rate was reduced by diluting the impregnating solution with the polymer. Details of the procedure and the apparatus are given.

Consolidation of Painted Wooden Artifacts

By E. Schaffer

Large numbers of artifacts in museum collections are made of wood and are frequently painted. The restoration of these objects often appears to be an impossible task from a technical point of view yet imperative, for with the declining interest of native ethnic groups in practicing their original art and craftsmanship they are irreplaceable.

This article describes the restoration of three painted wooden artifacts from the collection of the National Museum of Canada and discusses the general problems of conservation.

Decay of wood. The great strength of sound wood deteriorates rapidly under unfavorable environmental conditions. Biological agents such as fungi and wood boring insects at moderately elevated temperature in the presence of excessive moisture attack the cellulose-lingnin structure with a resulting decrease in mechanical strength. Cellulose fibres decompose also under the action of sunlight.

In the early stages of decay from sunlight yellowing is already apparent. This effect, in combination with rain, darkens several types of wood such as Engelman spruce a material widely used in the fabrication of Indian artifacts in Western Canada. Unfortunately this discoloration is caused by the near UV component of sunlight (3600-3950 Å) (1) which is not absorbed by the common window glass so that the process proceeds even indoors and the presence of excess moisture greatly aggravates

the situation. Thus biological degradation is always accompanied by discoloration of wood.

Somewhat unexpectedly radiation can also bleach certain types of wood, such as red cedar. When it is exposed to light of 4100 to 5200 Å wavelengths in the presence of moisture the impinging light is scattered by the detached fibres of the deteriorated surface and an impression of lighter surface color is created.

Problems associated with consolidation of painted articles. Modern polymer chemistry made it possible to consolidate wooden artifacts even in an advanced stage of decay, but protection of the paint film presents a problem. Certain polymers discolor. Others even dissolve the paint depending on the chemical composition of the pigment and medium.

The consolidation process usually darkens the wood; partly by the chemical effect of the agent and partly by alteration of surface texture. By drawing the detached fibres to the grain, impregnation eliminates light scattering at the fibre/air interface and therefore the surface color appears darker. In addition, the brown colored decay product often dissolves in the impregnating liquid and migrates from the interior of the wood to the surface. Because of this, the extent of discoloration on treatment is usually proportional to the degree of decay.

Another danger during consolidation is that the mechanical strength of a paint layer significantly decreases if the heat of the polymerization reaction is large and

differential expansion between substrate and paint occures.

Impregnation. Of course besides the difficulties associated with the presence of a paint layer, (also the general problems viz. impregnation of the article to a sufficient degree) initiation and completion of the polymerization reaction have to be solved.

The most effective and convenient method for impregnation is that *in vacuo*. If possible the permeating liquid optimally should have viscosity low enough for easy penetration but sufficiently high to prevent drainage during curing.

Catalyst. After impregnation the liquid has to be converted into a solid by polymerization. The reaction however is not spontaneous. For initiation the action of either radiation (2) or a catalyst is required.

The irradiation method has several advantages. The procedure is very simple, since the impregnated object has to be merely exposed to a Co-60 source. Usually this method yields also a high degree of polymerization. The reaction rate is easily controlled so that excessive warming on the liberation of the reaction heat (13 Kcal/mol for methylmethacrylate monomer) can be avoided. The great disadvantage of the method is a practical one, namely that for the provision of the radiation source involvement of an external organization is required, at that point the problems specific to conservation are often not sufficiently appreciated.

In contrast, the chemical catalysis method lends itself easily to laboratory application and renders good results

if properly designed. The catalyst to be preferred has a long shelf life when stored at room temperature and maintains a low polymerization rate. In this laboratory bis 4-t-butylcyclohexyl peroxidicarbonate (Percadox 16, manufactured by Noury Chemical Corporation) was found to fulfill these requirements.

Highly effective catalysts, which induce polymerization even at room temperature, are usually unstable, explosive, difficult to handle, and therefore poorly suited for conservation purposes. On the other hand the more stable catalysts require activation energy for initiation of the reaction. This the system can obtain from the surroundings in the form of heat (usually raising the temperature to 45 to 68°C is adequate) (3,4,5). Alternatively chemical activators may be utilized, which after forming unstable intermediate complexes with the peroxide catalysts breakdown, and render highly reactive free radicals (6) requiring no or small activation energy.

Since in the former mode the elevated temperature necessary for initiation rises further when the highly exothermic reaction proceeds, the temperature often becomes damagingly high and the use of activators would be generally preferred. On the other hand activators - such as tertiary amines for the polymerization of methylmethacrylate with peroxide catalysts - often discolor the polymer end product rendering it unacceptable for museum exhibition purposes. Thus, no universally applicable method can be recommended; the difficulties in each case have to be dealt with according to prevailing circumstances.

It was found in this laboratory that pyridine, as an

activator does not affect noticeably the color of the methylmethacrylate polymer catalyzed with Percadox 16, but it requires a slightly elevated temperature (35°C) for initiation. It has been used with good results as described below.

It should be emphasized that because oxygen of the air - similarly to hydro~~chinon~~quinone, phenol compounds, primary and secondary amines, copper ions etc. - react with the produced free radicals and thus prematurely terminate the polymerization reaction, impregnation of the artifact and the polymerization always has to be carried out in inert atmosphere (N_2 or CO_2).

Practical examples

The following three case histories from the National Museum of Canada may serve as illustrations for the applied restoration methods. All three objects from the Collection were very valuable study pieces and in an extremely poor condition. Added difficulty was that these wooden artifacts were painted and curators specifically prohibit inpainting on restoration.

Hawk (Cat.No. VII-D-126) (Figure 1) Painted wood carving made of pine 12 by 5 by 4 inches in size. Served as a roof decoration of a house in Bella Coola village British Columbia collected in 1920. The paint is applied over a gesso which according to X-ray fluorescence investigation contains salts of Sr and Ca, while the red ochre contains also Ba, Zn and Pb salts. The green colored area shows the presence of ZnO, $PbSO_4$ and $CaCO_3$ and traces of Cr and Fe, which suggests that the green pigment may be organic in nature.

The artifact was received in a deteriorated condition; he wood was badly weathered with little physical strength and aving lost much of the sound cellulose-lignin structure was xtremely light in weight. The wood had a grayish appearance. here was however no sign of the action of dry rot fungi or ood boring insects.

The object was placed in a vacuum chamber pumped for 0 minutes, and after flushing with nitrogen to remove the last races of adsorbed oxygen, impregnated in vacuo with monomer ethylmethacrylate containing 200 ppm hydrochinone stabilizer. The artifact was then left soaking for two hours under nitrogen tmosphere. The object was speedily transferred to a container, flushed with nitrogen, the nitrogen pressure increased to 1250 torr-in order to prevent drainage during irradiation - and the container sealed. The reaction was induced by gamma ray radiation of 1 Megarad (i.e. 10^8 erg/g absorption) from a Co-60 source of 20.000 curies. The treatment resulted in significantly increased mechanical strength of the frail, severely decayed wood. No undesirable change in the appearance of the wood occured; glossy surface film has not formed, the paint has not been attacked, in fact, its former dullness disappeared.

Panel (Cat.No. VII-X-1396) (Figure 2,3) 15 by 2.8 by ½ inch, the only remaining side of a destroyed box originating from the Far Northwest Coast of Canada and is estimated to be over 100 years old. The deep colored red ochre and carbonblack is applied onto the pine wood without undercoating. The design incorporates areas of unpainted wood.

Consolidation of this artifact presented one of the most difficult problems. Above all due to the action of fungi and wood boring insects the thin panel had become extremely fragile and powdery (It could not sustain its own weight and had to be kept in a tray). In addition, the consolidation treatment had to avoid not only attack of the paint but also darkening of the areas of the bare wood. Although the irradiation method rendered previously good results, in view of the seriously decayed state of this article further exploratory experiments were carried out on similarly deteriorated test pieces.

Penetration with the rather viscous Polyester Vibrin 117 (Uniroyal product) was found insufficient unless the system was subjected to several vacuum pressure cycles. In addition the process strongly discolored the specimens.

When the test pieces were soaked in a mixture of the monomer methylmethacrylate and 2% ethyleneglycol dimethylacrylate cross linking agent and exposed to gamma radiation under nitrogen atmosphere satisfactory increase of strength and negligible darkening was achieved. On subjecting the artifact itself to similar treatment the resulting consolidation was disappointingly low. It appears that although the liquid penetrated the wood initially it evaporated before polymerization took place. The vapor pressure of the liquid is rather high, even at room temperature 40 torr and increases rapidly as the temperature rises during polymerization. Oxygen could also have been present in adsorbed and absorbed state and contributed to the failure. At this point it was decided to defer the treatment of this

artifact until after the relative merits of the catalyst induced polymerization have been established.

Nootka wolf mask (Cat.No. VII-F-697) (Figure 4) Collected in 1950. Dimensions 19½ by 7½ by ½ inch. It was constructed from a single piece of pine wood painted with yellow, blue, black and red oil paint. Because preliminary tests revealed that this coat of paint is a latter addition applied over an earlier one which from an ethnographical point of view is more interesting, no pigment analysis was carried out.

One side of the mask was broken into several fragments and the wood due to the action of insects badly disintegrated.

Since vacuum impregnation appeared to be mandatory for successful impregnation a suitable apparatus had to be constructed.

The chamber (shown in figures 5 and 6) was of cylindrical shape, 19 inches in length and 9 inches in diameter. The removable end plate was sealed with a silicon rubber O-ring. The object to be impregnated was suspended in a stainless steel tray (19 by 8 inches) between a stainless steel wire mesh at the bottom and pins at the top. By this method sticking of the wood to the tray or floating on the surface of the liquid was avoided. The chamber was fitted with valves necessary for evacuation, transfer of the impregnating liquid to the tray and withdrawal from the chamber also with connections to a vacuum pump and nitrogen reservoir and vacuum gauge. Heating jacket surrounding the vessel was regulated with a temperature

controller (Figure 10, 11, 12).

Before impregnation, the object and liquid in the reservoir (Figure 7) (consisting of 1000 ml monomer 18 g Percadox 16 and 20 ml pyridine) were deaerated to a pressure of few tenth of a torr in order to remove the adsorbed and dissolved oxygen. Then, without breaking the vacuum, the solution was transferred to the chamber and the wood was allowed to soak in the liquid for 30 minutes under 1 atm. of nitrogen gas, after which the excess liquid was withdrawn. Finally, the system was left to consolidate for 24 to 36 hours.

Treatment of the first fragment yielded satisfactory increase of physical strength of the wood, however three or four hairline cracks formed in the paint which were assumed at first to be caused by shrinkage of the wood. It is known that the volume of methylmethacrylate decreases on polymerization by approximately 20% and, conceivably, this causes the wood to shrink and the paint film to crack. We found, however, that the contraction of impregnated wood on polymerization is less than 1% as determined by a Tuckerman optical strain gauge. This result suggested that cracking was caused primarily by the high temperature during the exothermic reaction and attempts had to be made to avoid it.

The logical step was to reduce the reaction rate. This was achieved by adding medium molecular weight polymer (Elvacit 2009 DuPont) in 10% concentration to the solution and decreasing the catalyst and activator content to 1%. To counteract the adverse effect of the reaction rate the retardation

temperature was raised to 40 to 45°C temperature after the completion of the initial stage of the reaction aiming to increase the degree of polymerization that is necessary for good physical strength. The temperature reached momentarily a peak of 117°C which perhaps is the optimum condition since at lower then 30°C temperature the reaction cannot be initiated. As was hoped, the paint remained unaffected by this treatment.

Panel treatment. After the successful application of the catalyst promoted polymerization in the consolidation of the wolf mask it was decided to apply the same process in the treatment of the panel instead of pursuing the gamma radiation method.

Because of its extremely poor condition the panel had to be strengthened at first to allow handling. The powdery weak parts were repeatedly brushed with a 20% polymer solution. Those areas which did not gain sufficient strength by this method were subjected to vacuum impregnation with the same solution. When all fragments were strong enough to be handled without danger they were treated as described in connection with the mask. The technique proved to be successful also in this case: the wood gained substantial physical strength without alteration of the painted surface. Only one minor problem arose: the unpainted areas became darker chiefly during the unsuccessful irradiation treatment and had to be slightly roughened with silicon carbide watersand paper.

Summary and Conclusion

The majority of pigments and their medium commonly

found on Indian artifacts are in general not attacked by methylmethacrylate monomer, although this has to be confirmed by exploratory tests before treatment of a given article. The composition of the impregnating liquid has to be so formulated that the viscosity should not be too high. The polymerization reaction can be induced either by gamma radiation or in cases of severely degraded objects by chemical catalysts. In order to avoid excessive warming during the reaction the rate has to be kept low. It was found that 4-t-butylcyclohexyl peroxidicarbonate gave satisfactory results when initiated with pyridine activator at 35°C. If the wood decayed to a powdery state brushing with polymer solution may lend sufficient strength for handling before and during vacuum impregnation. Exclusion of oxygen during all phases of treatment is imperative. No single technique for restoring artifacts seems to be universally applicable.

References

1. I.N. Stalker: Protection of timber from fire and weathering. Chemistry and Industry 1971, 1427.
2. A.E. Witt & J.E. Morrissey: Economics of making irradiated wood-plastic products. Modern Plastics 49, 78 (1972)
3. J.A. Meyer: Treatment of wood-polymer system using catalyst-heat techniques. Forest Product Journal 15, 362, (1965)
4. J.E.Langwig et all: New monomers used in making wood-plastics. Forest products Journal 19, 57, (1969)
5. J.F. Siau and J.A. Meyer: Comparison of the properties of heat and radiation cured wood-polymer combinations. Forest Products Journal 16, 47, (1966)
6. G.M. Brauer et all: Accelerating effect of amines on polymerization of methyl methacrylate. Modern Plastics 34, 153 (1956)
7. Franz Goetz: Methylmethacrylate fuer Einbettungen Fehlermoeglichkeiten und deren Beseitigung Praeparator Vol. 17, p. 83-88.

Un préalable à la restauration d'objets d'art ethnographique: l'étude anatomique des bois utilisés. Ses applications.

H. Van Geluwe

érêt de l'investigation des bois utilisés dans la sculpture des objets d'art ethnographique
ouble:

L'objet de cette recherche se justifie en soi

1.- elle permet de dégager les constantes (si constantes il y a !) dans la sélection des espèces utilisées;

2.- les normes qui régissent ces constantes procèdent de considérations soit
   a) techniques et physiques (propriétés physiques etc.):
      degré de résistance de la matière
      résistance aux agents exogènes: xylophages
                                      facteurs climatologiques
                                      température ambiante etc.
      soit
   b) culturelles ou socioculturelles:
      basées sur des propriétés magiques, attribuées à certaines espèces par sympathie ou par analogie
   c) ou de conditionnements (ou de limitations) écologiques ou phytogéographiques.

Les données fournies par l'étude phytoanatomique permettent des applications extrêmement utiles à l'évaluation anthropologique~~s~~

1.- par leur confrontation avec les informations recueillies par l'ethnographe sur place; correspondance et divergence entre les deux sont d'égale importance
   ex. stat. roi Kuba (ndop): informat.: ntul= pterocarpus; anal. phytoanatom.: ilunc= crossopterix febrifuga.

2.- la comparaison des identifications fournies par l'analyse anatomique avec les données phytogéographiques délimitant l'aire de répartition de l'espèce (ou sous-espèce) déterminée peut contribuer à localiser la provenance d'objets atypiques (ou aberrants) dépourvus d'indications - ex. masque Luba (dia.)

3.- l'identification phytoanatomique permet la détection de certaines falsifications:
   a) faux intégraux: ex. Buli (kambala: bois tropical commercial)
   b) altérations frauduleuse; ex. "maternité" Cokwe
                                   "fétiches à clou" Yombe
                                   siège à cariatide Luba
   c) restaurations abusives

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4.- utilisation de ces données pour la restauration (judicieuse), étude préalable des propriétés physiques (extension-contraction du bois sous l'action d'agents exogènes), choix du bois utilisé dans les restaurations.

"WOVEN BOUQUET"

DYESTUFFANALYSIS ON A GROUP OF NORTHERN DUTCH FLOWERED TABLECLOTHS AND TAPESTRIES OF THE 17TH CENTURY.

Judith H. Hofenk - de Graaff

INTERNATIONAL COUNCIL OF MUSEUMS / CONSEIL INTERNATIONAL DES MUSÉES
COMMITTEE FOR CONSERVATION / COMITÉ POUR LA CONSERVATION

PLENARY MEETING / RÉUNION PLÉNIÈRE

OCTOBER
2 - 5
OCTOBRE
1972

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CENTRAL RESEARCH LABORATORY FOR OBJECTS OF ART AND SCIENCE, AMSTERDAM

"WOVEN BOUQUET"

Dyestuffanalysis on a group of Northern Dutch flowered tablecloths and tapestries of the 17th Century.

Judith H. Hofenk de Graaff.

PRELIMINARY REPORT

Introduction

Dutch flowered tablecloths are very seldom since from the total production approx. 50 are left, being spread over several museums and private collections.

In 1969 and 1972 exhibitions were held of these tablecloths and tapestries, respectively in the "Danks Kunstindustri Museum" in Copenhagen and in the "Rijksmuseum" in Amsterdam.

Almost all remained tablecloths and tapestries were present at those exhibitions. To the most usual conceptions the flowered tablecloths and tapestries originate from the towns Gouda and Delft. The Dutch contribution to the history in tapestry-weaving started about the middle of the 16th Century. Many weavers from Flanders settled down in the Netherlands after the fall-down of Antwerp. Especially they did in the town Middelburg, Delft, Gouda and Schoonhoven. A summit on this was the work of Frans Spiering in Delft.

Many of the Dutch flowered-tapestries were made as per order and many tapestries especially were exported to Scandinavia, thus it is not surprising that about one third of the preserved tapestries and tablecloths remained there.

To their presentation the tapestries and tablecloths are very well to divide into a number of groups. Although it is very difficult to date the tablecloths and tapestries with certainty, some of them had the date woven in the board. In most, however, the date could not be fixed with certainty and thus they have to be temporarly dated between 1630 and 1670.

Aim of this Research

After having finished research on red-dyestuffs (period 1450-1600), turned out that a lot of data were missing, this with respect to origin and date was found out at the statistical process of the analysis results.

Owing to this it was impossible to give more than a rough estimation of analyzed results that have been obtained.

A possibility was created as to take samples of all tablecloths and tapestries since they were exhibited at the "Rijksmuseum" in 1972. Data fixed for the statistical process on the results of the analysis makes this group interesting enough as an object of research.

The tablecloths and tapestries are dated between 1630-1670, they originate from the Northern Netherlands, mainly from Delft and Gouda.

From the total stock of these tablecloths and tapestries were present at the exhibition in the "Rijksmuseum" in Amsterdam. The intention of this dyestuff-research will be, as to trace whether there would be a group of tablecloths that come e.g. from one workshop. This will be done by means of dyestuff-analysis and/or whether eventual specific mixtures of dyestuffs that might have been used.

Should it be possible as to prove by means of dyestuff-analysis that there are tablecloths and tapestries among them, that have been woven at a later date and according to the same cartoon ?!

Methods of Research

A thin layer chromatography was chosen for the analysis of dyestuffs in tablecloths and tapestries. In several previous researches this method has turned out to be the best for analysis of dyestuffs on textile materials. Samples are to be kept very small, so that no damage could be done to the object. It should be possible to work up a number of samples in a reasonable time.

Tentative summary of the results obtained so far.

Sampling

As far as possible from all tablecloths, tapestries and chair-coverings samples were taken from all colour shades. On chairs as well from the elbow-rest as the seats this was done.
From many tapestries often also the fringes were taken extra.
(Then these often are of a later date).

Results

On this very moment about 75% of all the samples are analyzed. With these analysis very soon it seemed that with the yellow, green and blue shades no spectacular results were achieved. Almost all the yellowed ones were dyed with weld;
the green ones with mixtures of weld and woad or Indigo. Although one may expect good results with the orange and red colours. Many mixtures were analyzed, and sometimes even with 4 different dyestuffs in it e.g. Madder + Cochineal + two kinds of redwood; or Brazil with weld. These mixtures are very well to be separated with T.L.C.

Only, after the statistical process of the results, we will be able to be more concrete in dividing the tablecloths and tapestries into groups of origins.

ICOM committee for conservation
Madrid 1972
~~Working-group "Water-logged wood"~~

Group 2/3

Derusting of iron drills found on sunken Dutch ships

T. Stambolov
and
E. Moll

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Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 16, Amsterdam
1972

Several of the large number of drills discovered on a sunken ship lying on an area gained from the sea (N.E. Holland) were submitted to the Central Research Laboratory for Objects of Art and Science, Amsterdam, with the request to subject them to various cleaning and preservation treatments. This was done in order to provide a better understanding of the influence of sea salts on the rust removal and conservation of corroded iron.

The derusting fluids used had the following compisition:

1) 3% of citric acid to which ammonia had been added in order to adjust the pH at 3.5 (KIRIYANOV, A.W. 'Restauration of Archaeological Objects' Akademii Nauk S.S.S.R., Moskow, 1960).
2) 5% of sulfuric acid to which 2% of inhibitor (arabic gum) had been added. (BURNS, R.M. and BRADLEY, W.W. 'Protective Coatings for Metals'. Reinhold Publishing Corporation, New York, 1962).
3) 250 - 500 gr. of orthophosphoric acid; 5 - 20 gr. of sodium carbonate; 3 - 10 gr. of zinc oxide; 0,5 - 2 gr. surfactant (LEROLAT 100 l. BAYER); 500 - 700 gr. distilled water (GIRAUD, V.C.M. French Patent 1242159 (30.12.1960).
4) 28,4% of Thioglycolic acid to which ammonia had been added in order to adjust the pH at 7. (KROCKOW, E.W. U.S. Patent 3,277,012 (4-10-1966).
5) 125 gr. of sodium hydroxide; 50 gr. of sodium gluconate; 1,5 gr. of surfactant (LEROLAT 100 l. BAYER); 825 gr. distilled water (REIDT, M.J. and TREVOORT, J.L.J., T.N.O. Publication - Delft, 126,4(1965).
6) Rainwater to which a fungicide (sublimate) had been added (LOBRY DE BRUYN, S.A. Bulletin en Nieuwsbulletin van de Ned. Oudheidkundige Bond, serie 6 Irq-1(1948), 23-21).

The drills were immersed in these liquids. Dailey they were taken out, inspected, the loose rust was brushed off and again immersed. The manipulation continued until complete derusting.

Liquids Nr. 4 and 5 delivered the best results. The rust removal was thorough without any attact on the metal itself. The other liquids either corroded the metal during dissolving of the rust layer or turned out to be insufficient rust removers. In all cases, mechanical cleaning prior to immersion increased greatly the speed of derusting.

Subsequently the drills were repeatedly washed off with distilled water and aceton with the purpose of removing any remnants of the cleaning fluid from them as well as drying them. The derusted and dried drills were then preserved by two treatments:
one group was immersed in molten ceresine, after about one hour taken out, and the excess of ceresine on the surface of the drills was discarded by rubbing it with cottonwoolpad soaked in toluene.
The other group was immersed in a formulation containing 5% ceresine and 5% ethylhydropolysiloxane in toluene again for about one hour, then taken out and left thus until the toluene has evaporated.

Several drills, after being mechanically cleaned from corrosion deposits that distorted their original form, were treated with rust stabilizers containing tannin. On the drills was, by way of a brish, first applied a solution of the following composition:
20 - 25% of tannin; 0,1% sublimate; 80 - 75% of distilled water; 150 ml/lt of alcohol (BLECK, R.D. Neue Museumskunde, 11, 4(1968), 489-491).
There followed an application, again by way of a brush, of a mixture containing 20% of the above mentioned tannin solution and 80% of polyvinylacetate (ISKRA, E.V. and SOKOLOV, G.M. Sudostroenie, No. 12(1965), 65-59).

The brushing of these compositions over the surface of the drills is indispensible as the stabilizing reaction between tannin and rust requires oxygen; a condition which excludes immersion. The soudness of this preservation method is still under study.

he International Council of
useums -
ommittee for Conservation

Conseil International des Musées
Comité pour la Conservation

Madrid: October 2-8, 1972

osef Riederer, Doerner - Institut, München.

CORROSION DAMAGE ON BRONZE SCULPTURES

he Clean - Air Commission of the Association of German Engineers as established a project to investigate damage caused by air ollution to men, animals, plants and materials. A working group f the section which investigates materials studies the corrosion f works of art. In 1969 the Doerner - Institute was charged ith the investigation of bronzes.

he first step made by the Doerner - Institute was to set up an nventory of all of the bronzes which are exposed outdoors and by hat endangered by an attack of aggressive components of the air. his inventory shows that in Germany there are three early portals n cathedrals, one from the 9th and two from the 11th century. he great sculpture of a lion at Braunschweig dates from 1166. rom the 16th and the 17th century there are about 100 bronzes, irst of all more than 50 sculptures at the Residence in Munich nd others at the famous fountains at Augsburg and Nürnberg. Only ive bronze monuments dating from 1625 to 1800 are outdoors. The ajority of monuments to sovereigns, to famous generals, artists r men of science was produced in the 19th century and at the eginning of the 20th century. From the 20th century there remain great number of works of sculptors, located mostly in the gardens f museums.

he second step, now knowing which bronzes are present in German owns, was to analyse the composition of these bronzes in order to ind out if there is a dependence of corrosion upon the content of opper, tin, zinc, lead or some other element present in minor ercentage. We analysed all early bronzes which could be reached n order to the samples. This study revealed a lot of interesting echnical observations about the casting of bronzes in the 16th entury, especially the fact that different alloys were intentionally chosen. For instance, there is the fountain dedicated to the oman emperor Augustus at Augsburg, which is named after him. At his fountain, on four levels figures occur with different

ompositions. The first series is made of brass, with 80% Cu, 16% n and 3% Pb, the second is made of an alloy with 86% Cu, 7% Zn, % Sn and 3% Pb, the third series and the figure of the emperor on he top of the fountain are made of bronze with 90% Cu, 5% Sn and % Pb. Other monuments, cast by gun founders consist precisely of un-metal with 90% Cu and 10% Sn. In the Residenz at Munich there re bronzes containing more than 10% Pb.

he analysis of the later bronzes showed that already by the eginning of the 19th century alloys were used for casting monum-nts, which contain besides copper 6 - 10% Sn, 4 - 7% Zn and small mounts of lead.

his great variety of compositions had to be considered, when eeking the cause of different appearances of corroded bronze culptures.

The third point which was examined, was the location of the bronzes with relation to the extent of air pollution by sulfur dioxide and dust in urban areas.

For instance, at Munich, where the air's content of gases and dust is measured regularly at a great number of points, we know that the pollution with SO_2 is highest in the center, diminishes gradually to the suburbs and disappears completely at the belt of forests around the town. But the same is true of bronzes, which too are concentrated in the center and their number decreases rapidly toward the borders of the town. In particular, the bronzes of the 16th century are in the very center of the town in their original positions.

The fourth point of investigation was a study of the corrosion products on the bronzes. The identification was done by X-ray diffraction powder - patterns, a rapid and routine method, so that more than 500 samples from all parts of Germany could be examined. It was found that the most frequently occuring green corrosion product is the basic copper sulfate brochantite, $CuSO_4 \cdot 3Cu(OH)_2$. The basic copper sulfate antlerite $CuSO_4 \cdot 2\ Cu(OH)_2$ occurs rarely. The copper sulfate $CuSO_4 \cdot 5\ H_2O$ was found only a few times, forming blue crystals. Occurrence of basic copper chlorides could always be explained by an attack of water rich in chlorides. Basic copper nitrates proved to be an artificial patina. Dark copper sulfides, which were mentioned frequently in older literature could never be identified.

in alters to metastannic acid H_2SnO_3, which can be found on X-ray
iffraction powder patterns, but which is more rapidly removed by
ain. On bronzes rich in lead, white lead sulfate occurs and leads
o a grayish appearance of the object. Bronzes rich in lead dis-
ntegrate rapidly, for lead is not soluble in copper and tin, but
orms seperate nodules, so that electrochemical processes contrib-
te to the dissolution of the less noble lead.

dventitious compounds of the crust found on the surface of the
ronze, not due to the decomposition of the bronze, are iron
xides from the ash of combustion, quartz from dust and what is
otable because of its dangerous effect on the bronze, great
mounts of gypsum. Gypsum is formed by the action of water rich
n SO_2, transforming the calcium - carbonate, which is present
n the urban dust up to 30% into the calcium sulfate. Gypsum
ardens the dark crust on the bronze and, forming crystals of
ome milimeters in length, makes the surface rough, so that new
ust can be deposited easily.

he metallographic examination of cross sections made through the
rust of dirt, the patina and the metal revealed a situation
raught with danger for the bronze.

ver the metal occurs a layer of red cuprous oxide. Above that
ollow the green corrosion products. Neither red nor green patina
an be considered as protective layers merely buried under the
rust of dirt. They are aggressively proceeding fronts of
estruction, which penetrate into the metal all the more rapidly
if the attacking water contains sulfur dioxide or if the absorbent
rust of dirt is rich in aggressive compounds. By this mode of
ecomposition, which proceeds slowly but continuously, the surface
f the bronze is eroded only about one millimeter or less in one
entury, but that was enough to destroy from 16th century sculptures
the cold worked, punched and chased ornaments. With them a great
eal of the original evidence that they were masterpieces has been
lost.

Over the red and green corrosion products we find a sequence of light and black layers, which mark the dusty precipitations during the summer, followed by the soot of the heating period in the winter.

lthough the corrosion of bronzes is due to sulfur dioxide in the ir and the soot of combustion, the attack on bronzes is not ntirely a phenomenon of our time: it had already started in the arly 19th century. From that period there remain the description f unpleasant change in the appearence of monuments of the same ind as we observe today, when within a few years metallic bronzes ecome dark and ugly.

ow, knowing the variation of the composition of the threatened aterial, the aggressive components of the air, and the causes f corrosion, we could begin the study of materials for the rotection of bronzes.

s protective coatings of recently cast or old cleaned bronzes, ils, waxes and synthetic materials are being proposed.

ils and waxes, which have been used for the protection of bronzes or a long time, have the disadvantage, that they are efficient nly for a short period, then they have to be applied anew. The ost and man power thereby required for the maintenance of all the ronzes of a town, deters the responsible authorities from agreeing o regular treatment. They still rely on their belief in bronze as resistant material. The great advantage of oils and waxes as rotective coatings is: first, the agreeable and pleasing surface hich is attained by their use and second, the ability to apply hem without difficulty also to patinated bronzes.

oatings of synthetic materials are much more durable. New bronzes ertainly can be protected for many years without any change of heir surface. For older bronzes, whose appearance is determined y a natural green patina and the black crusts of soot, synthetic aterials are less useful.

To find out the most efficient among all the lacquers offered by industry, we sent a description of our problem to 80 producers of metal lacquers in Germany, asking them to provide us with samples for test applications. 36 firms were able to send us one or more lacquer of their own production and with five exceptions all revealed the kind of synthetic resin that was the base of the lacquer.

The lacquers belong to the following groups:

Acrylic	17

olyurethan	9
lkyd	2
poxy	3
olyester	2
VC / PVA	1
ombinations	3
nknown	5

o test the efficiency of these coatings of synthetic materials, ils, waxes and some other processes, 9 plates of bronze, 10 cm x 5 cm and of a particular shape, were cast with an alloy which is actually used for casting outdoor bronzes. These pieces were protected with 42 lacquers, 12 waxes, 4 oils and 2 fats. One group which was not coated is regularly cleaned with water, containing different admixtures. On ten pieces a brown artificial patina was produced and then coated with waxes, oils and lacquers. All pieces were partially treated with benzotriazol as a corrosion inhibitor before the application of the lacquers. On six pieces other inhibitors are being tested.

81 of these pieces, all treated with different products, are exposed to natural weathering and the attack of aggressive components of the polluted air at the Doerner - Institute in Munich, which is located in the center of the town, where the highest concentrations of SO_2 were determined (1965: 40 mg SO_2/100 m^3, 1969: 15 mg SO_2/100 m^3. The considerable reduction of SO_2 in the center of Munich indicated here is due to the efforts of the municipal administrations, especially the introduction of clean fuels.).

At the same time, streaks 5cm x 15cm of the same protective materials were applied to sheets of bronze, copper, brass, aluminium and steel of the sice 100 cm x 60cm x 2mm to test their adherence on very smooth surfaces.

Small strips of copper with and without treatment with benzotriazole were coated with all of these materials, to use them for an accelerated weathering test.

For the microscopic examination of the gradual decomposition or alteration of the coating materials, 600 small protected plates are being exposed at this point in the center of Munich.

Parallel to the test-series to find out the efficiency of various coatings an exposure test is being run to investigate the alteration of different copper alloys in different surroundings. Pieces of the same shape as those used for coating were cast of five different alloys:

		Cu	Sn	Pb	Zn
1.	Rg 5	85	5	3	7
2.	Rg 9	87	9	–	4
3.	GBZ 10	90	10	–	–
4.	GBZ 14	86	14	–	–
5.	Lead bronze	72	10	8	–

These, together with one copper sheet and one brass sheet, are exposed at places with different amounts of SO_2 and dust in the air.

The following points have been chosen:

		SO_2 (mg/m3	dust (g/m^2/month)
1.	Center of Munich	0.20 – 0.70	8
2.	Industrial region of Munich	0.15 – 0.70	11
3.	Suburb of Munich	<0.01	–
4.	Forest near Munich	<0.01	–
5.	Mountain in the Alps	<0.01	–
6.	Herten (industrial region, NW Germany)	0.20 – 0.40	20
7.	Essen (industrial region, NW Germany)	0.20 – 0.40	20
8.	Duisburg (industrial region, NW Germany)	0.39 – 0.75	60

Photographs were taken of all objects before exposure. Photomicrographs were also made at specific points of most of them. These photos will be repeated in regular intervals so that any alteration of the surface is documented.

This project of exposing bronzes protected by different coatings has been running only since March 1972, so that it is not yet known which materials withstand the test, but we do have sufficient experience in applying these materials. From this we have been

able to proceed to the conservation of one of the most important bronze sculptures still outdoors in the center of Munich, the sculpture of the archangle St. Michael dating from 1588. The thick crusts of dirt were removed mechanically, in some places down to the green patina to avoid a spotty appearance and finally it was treated with a solution of waxes, which can be renewed if necessary. On the reverse side of the sculpture which cannot be viewed, one part was coated with an acrylic resin which had shown good properties when applied on test sheets.

By the next meeting we shall have observed the durability of these materials used for exposure tests, but too we shall continue to protect old and new sculptures, always applying methods which proved to be efficient, in order to enlarge our experience on this field too.

References:

Riederer, J.: Die Zerstörung von Kunstwerken durch luftverunreinigende Stoffe. Schönere Heimat, 6/, pp 44 - 47, 1971.

Riederer, J.: Korrosionsschäden an Kunstwerken.
Baumeister, 68, pp 1202 - 1206, 1971.

Riederer, J.: Kunstwerke in Gefahr. Einflus der Luftverunreinigung auf die Kunstdenkmäler Münchens.
Technik und München, 1971, pp 228 - 231.

Riederer, J.: Die Einwirkung luftverunreingender Stoffe auf Kunstwerke aus Bronze. Report for the DFG, 89 pag.

Riederer, J.: Die Konservierung von Bronzeskulpturen.
Restauro, 1, pp 40 - 41, 1972.

Riederer, J.: Korrosionsschäden an Bronzen der Münchner Residenz.
Deutsche Kunst - und Denkmalpflege, H.1, 1972.

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ICOM COMMITTEE FOR CONSERVATION, MADRID, OCTOBER 1972

The Interaction Of Benzotriazole With Copper Compounds

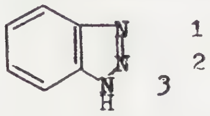
The possibility of using benzotriazole to treat copper alloy jects affected with "bronze disease" was recognized shortly after blication of articles by Cotton (1,2) and by Prall and Shreir (3,4). lsen published the first report on the use of benzotriazole in servation in 1967 (5), and has recently published a second report(6). skuil (7) has commented on the second report in a letter. In a com- nion report to the Working Group on metals, Virginia Greene (8) has ported a series of experiments which provide information about e behavior of benzotriazole under conservation laboratory conditions.

This report reviews the literature on the interaction of ben- triazole with copper surfaces and copper chemicals as a background r a study of the interaction of benzotriazole with the copper com- unds found in patinas on bronze objects, and reports on experiments w being conducted.

Benzotriazole is currently in use to inhibit the corrosion of pper and copper alloys in a considerable number of industrial and mmercial applications spanning a wide range of conditions. The ficacy of benzotriazole, alone or with other substances, for the otection of copper seems well established and is documented ex- nsively in technical and scientific journals as well as in the patent terature. This literature has been reviewed in industrial tech- cal and applications bulletins (9,10), from the early patents through out mid-1968 and more recently by Hori (11) and Walker (12). A ief review of additional and more recent applications articles l patents is presented in an appendix to this report which is con- rned principally with patinated objects.

Benzotriazole was first characterized by Ladenburg (13) in 1876. er (14) has surveyed the chemistry of benzotriazole and related sses of compounds to about 1960. The physical properties of benriazole are adequately tabulated in handbooks (15) and in applicans literature (9) and need not be repeated here. A comprehensive vey of the chemistry of benzotriazole and the substituted benzotriaes since 1960 would be many times the length of this report and h would appear to be far afield from the interests of workers in servation. A number of substituted benzotriazoles, however, have n screened for usefulness in inhibiting copper corrosion. Some are covered by specific patents for such use. The more recent of these included in the appendix.

Benzotriazole was of interest to chemists from the outset since is a model or parent compound for whole sequences of compounds, y of which are similar to physiologically active, naturally occuring pounds. Benzotriazole, often represented structurally as



been shown to have a multiple bond character between the 2- and positions equivalent to that between the 1 and 2- positions milar to the situation in the benzene ring). The weakly acidic rogen, shown in position 3, may be on either position 1- or 3-*(16). h nitrogen (including the one shown with the hydrogen) has an hared electron "lone" pair. An alternate, more symmetric repre-

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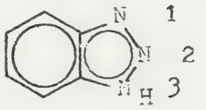
*The hydrogen may also be thought of as being on the 2- position a small fraction of the time. There is an important family of plexly substituted benzotriazole aromatic 2- derivatives in use as stuffs, fluorescent whiteners and as protective agents against ultralet radiation.

ation, stressing the coequivalence of bonds and positions would be



.

, benzotriazoles may function as weak acids (releasing the hydro-
from the 3-(or 1-) position) or as bases, accepting a hydrogen
one of the nitrogen "lone" pairs (17). Benzotriazole may also
olve these "lone" pairs in bonds to other species, including, of
rse, copper ions.

The weak acid character of benzotriazoles was recognized early
was the accompanying ability to form metal salts [*], although the
st literature report of such a metal salt of benzotriazole noted
Beilstein, a white silver salt, was that of Elbs (23) in 1924.
is usually stressed, explicitly or implicitly, that this is the mode
interaction of benzotriazole with copper ions (an exception to
s is the work of Prall and Shreir (4) on copper(I) ion.

Much of this frequently cited literature relevant to this re-
t concerns attempts to interpret the interaction of benzotriazole
h a copper surface (or a copper(I) oxide covered surface). It seems
be generally agreed that the materials formed on a copper surface

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[*] In 1888, shortly after the preparation of the parent com-
nd, the bromine derivative, 5-bromobenzotriazole was observed to
m a white sodium salt, a white silver salt, and a green copper salt
well as white salts of zinc, cadmium and mercury(18). Analyses were
orted for the sodium and silver compounds which were consistent
h a 1:1 formula for metal:substituted benzotriazole anion, $C_6H_3BrN_3^-$.

This series of reactions resulted in later work by Tarasevich and
coworkers (19-22) who investigated 5-bromobenzotriazole (and ben-
riazole itself) as a possible precipitating agent for the gravimetric
ermination of metals, chiefly silver and copper.

relatively insoluble, tend to protect the surface from tarnishing
nough not from attack according to Mansfeld, Parry, and Smith (24),
a film and/or are polymeric and are copper(I) - benzotriazole
rials. The surface material is not generally formed in sufficient
tity to harvest and examine directly. The surface work is summarized
able I.

In attempts to gain further information about the materials pro-
ing a copper surface, Cotton and his coworkers (1,2,26), Prall
Shreir (4,25), and Poling (27), and Morito and Suetaka (28) have
ted aqueous benzotriazole with copper(I) and copper(II) compounds
aqueous solutions producing a number of copper-benzotriazole
rials.[*] Additional information can be derived from the literature
nalytical chemistry, since benzotriazole has been used as an
ytical reagent for copper and silver. Some copper-benzotriazole
ounds have been synthesized and characterized for studies of mag-
c susceptabilities. This work above is summarized in chronological
r[**] in Table II.

[*] Copper, Cu, has an electron configuration $(4s)^2(3d)^9$. Copper I
uprous ion, Cu^+, is assigned an electron configuration $(4s)^0(3d)^{10}$.
cuprous salts might be expected to be diamagnetic and to resemble
logous silver salts in being white or palely colored. Copper (II)
upric ion, Cu^{+2} is assigned an electron configuration $(4s)^0(3d)^9$.
cupric salts would be expected to be paramagnetic, and colored,
mbling transition metal salts. There are instances of substances
similar assigned electron configurations which contain metal-
l bonds and have different magnetic susceptabilities than would
redicted from the simple models above.

[**] It should again be noted that there is a large applications
rature describing immersion and polarization tests and specu-
ng on a mechanism for protective action but not describing
tion products. This material is summarized by Walker and in
ier reviews.

TABLE I

REACTIONS BETWEEN COPPER METAL SURFACES AND BENZOTRIAZOLE

AUTHOR AND REFERENCE		COMPOUNDS CLAIMED AND CONDITIONS
Prall Prall and Shreir	25 3,4	CuBTA, working with acid (pH = 1) plating solutions containing sulfate ions, 1% BTAH, resulting in codeposits, from which BTAH could be recovered; no proton loss.
Cotton Dugdale and Cotton Cotton and Scholes	1 2 26	CuBTA, in thin layers, many sets of conditions, representative set: 2 min. exposure, to 0.25% aqueous BTAH; pH = 6-7; at 60 C, methods include infrared reflectance spectroscopy and ellipsometry. Proton loss.
Poling	27	CuBTA, in layers which could become quite thick, 1 1/4 hours, 3% NaCl, 0.02 M BTAH; pH = 3; at 26 C, H_2 purged solutions. Many other sets of conditions said to provide similar results. Infrared reflectance spectroscopy. Proton loss.
Mansfield, Smith and Parry	24	CuBTA in thin layers, 24 hr., 5% NaCl, 1% BTAH, 50 C, also other conditions. Immersion tests, ellipsometry, AC impedance measurements, potentiostatic polarization measurements.
Morito and Suetaka	28	CuBTA in thin layers, 20 hrs., 3% NaCl, 0.02 M BTAH; pH = 3; 25 C Infrared and UV-visible reflectance spectroscopy. Proton loss.
Angely, Bonnemay, Bronoel, and Peslerbe	29	Benzotriazole, in the gas phase, in an argon stream interacting with copper. Results indicate each BTAH molecule reacts with two sites on the copper surface.

TABLE II - 1

REACTIONS BETWEEN SALTS OF Cu(I) AND Cu(II) AND BENZOTRIAZOLE(1)

Author(2)	Reference	Date	Compounds Claimed, Properties, pH Ranges, Remarks
Remington (A)	30	1937	Cu(I) yellowish white precipitate from acid solutions, blue precipitate from alkaline tartrate solutions. Precipitation from ammonium acetate buffer solution hot, with 2% BTAH under reducing conditions, produced a material with a CuBTA stoichiometry. Cu(II) green precipitate from acid solution, blue precipitate from alkaline tartrate solution.
Curtis (A)	31	1941	Cu(II)BTA_2, blue green from ammonical solutions, pH = 7-8.5, does not form below pH = 5, and dissolves above 8.8. Acetic and tartaric acids present. Percentage of Cu in good agreement with formula.
Tarasevich (A)	19	1948	Cu(II) reported to interfere with tests for Ag^+ in acid solution (pH = 0.3 with HNO_3) unless separation procedures are employed.
Cheng (A)	32	1954	Qualitative tests on Cu(II) showed a yellowish green precipitate from ammonical solutions, no precipitate from ammonical Versenate solution. Cu(I) did not precipitate from

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(1) Film results on copper metal are not included.

Benzotriazole $C_6H_4N_3H$ = BTAH, $C_6H_4N_3$ = BTA^-

TABLE II - 2

Author	Reference	Date	Compounds Claimed, Properties, pH Ranges, Remarks
Cheng (continued)			ammonical Versenate solution.
Canonica, De Leone, and Bersano (P)	33	1954	Cu(BTA)OAc, $Cu(BTA)_2 \cdot 2H_2O$ and perhaps others, all are paramagnetic.
Tarasevich (A)	20	1955	$Cu(II)BTA_2$ by homogeneous precipitation from a warm solution slightly acid with acetic acid.
Lomakina, Tarasevich and Agasyan (A)	22	1957	Cu in large excesses interferes with the micropotentiometric procedures for silver in 0.05-0.1N HNO_3 because a slightly soluble complex separates even in weakly acid solutions.
Prall (M)	25	1962	Thesis (See Prall and Shreir, 1964) Cu(I) (formed by reduction of aqueous $CuSO_4$) yields a gelatinous khaki colored precipitate at pH = 0.2 in presence of NH_4^+. pH titration Cu^+ ions at initial pH = 4.5 did not indicate proton release. Cu(II) (aqueous $CuSO_4$) yields a turquoise precipitate at pH = 2.5. No precipitate observed at pH = 2.0. pH titration with Cu^{+2} ions at initial pH = 4.5 indicates proton release equivalent to 2BTAH protons per Cu^{+2} ion.
Cotton (M)	1	1963	Cu(I)BTA, yellow or lime green from CuCl in near neutral solutions, stoichiometrically correct for 1:1 metal:BTA based on analysis for C, H, N, diamagnetic, amorphous. Composition

TABLE II - 3

Author	Reference	Date	Compounds Claimed, Properties, pH Ranges, Remarks
Cotton (continued)			on temperature and mode of precipitation. Formula not assigned. Compound crystalline. Composition of Cu(II) material from near neutral sulfate solution close to stoichiometric agreement for $CuBTA_2$ but esr data indicate that material is not a normal copper(II) derivative. Material is amorphous or microcrystalline.
Prall and Shreir (M)	4	1964	Cu(I)BTA, formula certain, from solution pH = 0.2-2.5 very strong acid required to dissociate to Cu(I) and BTAH; $Cu(I)BTA \xrightarrow[H_2O]{O_2} Cu^{++}$ + BTAH; soluble in pyridine, insoluble in disodium EDTA. Proton release claimed.
Akiyama and Terano	34	1964	$Cu(II)BTA_2$, blue, pH = 4.4-4.6 (Cu determined as CuO). No precipitate in pH range 2.6-2.8 or less, recovery of Cu(II) drops off below pH 7.
Inoue, Kishita, and Kubo (P)	35	1965	Cu(II)(BTA)Cl, yellow green from ethanol-BTAH solution. $Cu(II)BTAHCl_2$ yellow brown crystals from Cu(II)BTACl re-crystallized in 4N HCl, decomposes in water.
Cotton and Scholes (M)	26	1967	(Related to Cotton, 1963) $BTA_4Cu_3Cl_2 \cdot H_2O$ or $CuCl_2 \cdot (CuBTA)_2 \cdot 2H_2O$, crystalline from aqueous near neutral chloride solutions. $(BTA_2Cu)_3 \cdot 2H_2O$, amorphous from aqueous sulfate solution. Both are dark green. Cu(I)BTA amorphous but of certain

TABLE II - 4

Author	Reference	Date	Compounds Claimed, Properties, pH Ranges, Remarks
Havíř (A)	36	1967	Reaction with Cu(I) gave precipitates at pH of 3 (hydrogenphthalate buffer), 7 (ammonium acetate buffer), and 10 (glycine buffer) (assumed colorless from text) as did Cu(II) at same pH's (assumed to be green from the text).
Gerenrot and Eichis (M)	37	1968	[$(Cu(I)BTAH)_2SO_4$ and $Cu(II)BTAH_2SO_4$ postulated on basis of Prall and Shreir]
Poling (M)	27	1969	Cu(I)BTA, pH = 1.0, Ar purged aqueous solution. Density 1.65; light yellow to green, some Cl^- retained, variable magnetic susceptibility, pyridine soluble, insoluble in many organic solvents. IR indicated proton loss, soluble in di-NaEDTA slowly, Cu(II) compounds, variable composition from chloride and sulfate solutions as described by Prall and Shreir.
Poddar and Roy (A)	38	1970	Amperometric titrations in an acetate buffer pH = 6 show a break for Cu(II) at 1:1 ratio i.e. suggest Cu(BTA)OAc as an insoluble precipitate (not described)
Morito and Suetaka	28	1971	IR and UV-visible studies of materials similar to those prepared by Cotton and by Poling; N-H bond lost.

Although a copper(I) benzotriazolate (CuBTA, $CuC_6H_4N_3$) and a
r(II) benzotriazolate ($CuBTA_2$, $Cu_2(C_6H_4N_3)_2$) are known from
es of benzotriazole as a precipitation agent, it would appear
copper(I) and copper(II) substances can interact with benzo-
zole to yield a number of materials, some of which may be mixtures.
naterials formed from copper(I) substances seem less soluble in
r, in acid, in organic solvents, and in complexing agents than the
rials formed from copper(II) substances. However, since the
rials resulting from the copper(I) substances are yellow-green
reen, rather than the anticipated white to yellow in color, quite
ably a considerable fraction of copper(II)-benzotriazole inter-
on products are present, due to air or auto-oxidation of copper(I)
he presence of moisture. Particularly in the case of copper(II)-
otriazole interaction, it would appear that different materials
mixtures) may be obtained with changes in starting materials,
ent, pH, or of ligands present (as supplied by buffers).

This report, to this point, supports and extends the observa-
s of Virginia Greene in sections I and II of her report. Hopefully,
nswers some of the questions she has raised. Certainly it under-
res her concern that different products may be observed with a shift
solvents or a shift in starting materials, which, in the conservator's
, are the patination compounds. The balance of the report briefly
lines work presently in progress or projected to resolve some of
remaining questions concerning the interactions of benzotriazole
n copper corrosion products, and the characterization of the materials
ned under conditions similar to those found in or on an object, and
conservation practice. It should be acknowledged at the outset that

erent materials may be obtained in rather similar appearing sets
ircumstances, that mixtures rather than single substances may often
lt, that, particularly in the case of mineralized patinas, the
tion may be a surface reaction. If such materials can be characterized
prepared reproducibly, simulated aging and related experiments
be carried out.

The work underway attempted:

1) to characterize the materials observed in the experiments of Virginia Greene (part III, 3) using solutions of benzotriazole in water and ethanol with solid copper(I) chloride, copper(II) chloride, and copper(II) sulfate.
2) to characterize the reaction products and extent of reaction of benzotriazole in water and ethanol with finely divided synthetic copper corrosion products, copper(I) oxide, copper(I) chloride, the copper basic chlorides (paratacamite and atacamite), a copper basic carbonate (malachite), and with copper(II) chloride dihydrate.
3) to carry out experiments to determine the nature and extent of interaction of benzotriazole in water and ethanol with corroded copper plates and with mineralized patina substances (initially malachite and cuprite).

h of the working period was consumed in the calibration of
truments and in the preparation of standards. The balance of the
k, presented here, represents tentative working conclusions, pending
ther work, particularly chemical analyses. The work under headings
and 2) above are, of course, closely related and have in practice
ome interdependent. Concerning 1) it should suffice to say that
have repeated the test-tube experiments of Virginia Greene

eral times and concur with her observations as presented earlier.
cerning 2), we have worked with solid synthetic copper corrosion
ducts (and copper(II) chloride dihydrate) and benzotriazole
bratec 99, as supplied by the Sherwin-Williams Company, and re-
stallized Eastman Kodak P2759) in water and in ethanol (95% grain
ohol). In general, about 0.001 mole of the copper substance was
ced in contact with benzotriazole in sufficient amount to supply
benzotriazole molecule for each copper valence unit (e.g. Cu(I):BTAH;
II):2 BTAH). The usual volume of liquid was 50 ml. The pH of the
tures was monitored* and the systems were observed visually until
further changes were observed and pH became constant. The resulting
lid materials were collected and washed with water or ethanol.
ray diffractometer scans of the solids were made. We project
amining these solids by infrared reflectance spectrometry, but are
ill in the stage of developing and adapting techniques and standards
r this problem.

PPER(I) OXIDE, Cu_2O, CUPRITE

pper(I) oxide slurried in water or in ethanol manifests a pH
ightly higher than the solvent (+0.2 pH unit, relative to distilled
ter, +0.1 pH unit, relative to ethanol). The copper(I) oxide is not
sually changed after extended slurrying in water-benzotriazole
ethanol-benzotriazole. Final pH is slightly lower than that of
nzotriazole in water and slightly higher than that of benzotriazole
ethanol (-0.3, +0.3). No new diffraction peaks were observed and

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alues of pH in ethanol solutions must be interpreted with caution and
ust not be directly compared with water system values.(39) Changes
ay be interpreted in the same way one would interpret similar changes
n a water system. For that reason changes are reported here.

evidence of amorphous or ill-crystallized material was noted.

PER(I) CHLORIDE, CuCl, NANTOKITE

per(I) chloride slurried in water or in ethanol with no attempt to lude oxygen begins to change in appearance and to oxidize to form per(II) ion. The final pH of the slurry is slightly higher than solvent in the case of water (+0.1) and is lower than the solvent the case of ethanol (-0.2). An olive green material or materials ult with benzotriazole in both water and ethanol. The conversion the copper(I) chloride does not appear visually to be complete either case. Final pH indicates considerable proton release or mation in water (-3.3, relative to benzotriazole in water) and in anol (-3.0, relative to benzotriazole in ethanol). Diffraction ks of copper(I) chloride are observed in final material and no peaks were observed.

PPER(II) CHLORIDE DIHYDRATE, $CuCl_2 \cdot 2H_2O$

pper(II) chloride solutions are relatively acidic due to solvolysis 2.2, -6.4 relative to solvent). Interaction in solution with nzotriazole yields a green material (and, in the proportions ed, a green solution, indicating that not all the copper was moved from solution). Final pH indicated proton release or for- tion in water (-3.1 relative to copper(II) chloride in water, -2.3 lative to benzotriazole in water) and a more complex situation in hanol (+0.5 relative to copper(II) chloride in ethanol, -4.2 relative benzotriazole in ethanol). Diffraction results for the water stem indicates amorphous material and for the ethanol system results cw copper(II) chloride, benzotriazole and some new peaks.

ER(II) BASIC CHLORIDE, $Cu(OH)_3Cl$, PARATACAMITE and ATACAMITE*

rries of paratacamite are relatively acidic (-1.0, -3.2). Benzo-
zole in water and in ethanol produces new green materials in both
es but does not appear to produce complete conversion. Final
ndicates proton release or formation in water (-2.5 relative to
otriazole in water) and in ethanol (-2.4 relative to benzotriazole
thanol). Diffraction results for the water system are generally
rphous with some benzotriazole peaks and some unidentified peaks.
fraction results for the ethanol system show paratacamite peaks
well as a number of unidentified peaks. The materials from the
systems may be different.

ervations on atacamite are similar to those for paratacamite.
version is not complete and atacamite peaks remain in the
fraction scans and some unidentified peaks are observed.

PER(II) BASIC CARBONATE, $Cu_2(OH)_2CO_3$, MALACHITE

rries of malachite are relatively basic (+1.5 relative to water,
9 relative to ethanol) Benzotriazole in water and in ethanol
duces new green materials but does not result in complete con-
sion. Final pH is higher than with the paratacamite or atacamite
tems (+0.6 relative to benzotriazole in water, and +1.0 relative
benzotriazole in ethanol). Diffraction scans for the water
tem are essentially amorphous with small peaks suggesting malachite
benzotriazole as well as some unidentified peaks. Diffraction
ns for the ethanol system are also amorphous and show no new peaks.
overall extent of conversion does not seem as great as for the
per(II) basic chlorides. No evolution of carbon dioxide was noted.

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e paratacamite and atacamite used in this study were prepared by
e methods described by Lewin and Sharkey (40).

ummary, in stoichiometric quantities (based on the postulated
lete conversion of copper to copper(I) benzotriazolate or
er(II) benzotriazolate) and with stirring, benzotriazole in
r and in ethanol shows little conversion of copper(I) oxide and
mplete conversion of copper(I) chloride, of the copper(II) basic
rides, and of copper(II) basic carbonate, although in all the
er cases some conversion to new relatively insoluble green materials
lts with the formation of a relatively acid solution. It may be
umed that in the case of copper(I) oxide the material(s) postulated
he copper studies has been formed on the surface. In poorly
red or compacted samples and for these materials in mineralized
it would be presumed that interaction would be restricted to
ssible surfaces which would become coated with benzotriazole in-
ction products.

ected work includes the repetition and extension of the above work
attempts to separate the solid phases and to characterize them by
y diffraction and chemical analysis. Characterization of new
rials by means of infrared reflection spectroscopy will be
mpted. Work with corroded copper plates and mineralized and
acted copper compounds will be attempted to determine the extent
enzotriazole conversion of such materials.

REFERENCES

Cotton, J.B., 'Control of surface reactions on copper by means of organic reagents'. Intern. Congr. Metal Corrosion, 2nd, New York City 1963 590-5, discussion 595-6 (Pub. 1966)

Dugdale, I.; Cotton, J.B., 'An electrochemical investigation of the prevention of staining of copper by benzotriazole.' Corrosion Sci. 3 (2), 69-74 (1963)

Prall, J.K.; Shreir, L.L., 'Effect of codeposited material on the corrosion behavior of electrodeposits.' Corrosion Sci. 1 181-2 (1961)

Prall, J.K.; Shreir, L.L., 'Benzotriazole as an addition agent for acid copper in solution'. Trans. Inst. Metal Finishing, 41 (1), 25-39 (1964)

Madsen, H. Brinch, 'A preliminary note on the use of benzotriazole for stabilizing bronze objects'. Stud. Conserv. 12 (4), 163-167 (1967)

Madsen, H. Brinch, 'Further remarks on the use of benzotriazole for stabilizing bronze objects'. Stud. Conserv. 16 (4), 120-122 (1971)

Voskuil, J., Studies in Conservation 17 (1), 44 (1972)

Greene, Virginia, The use of benzotriazole in conservation: problems and experiments, presented to Working Group on Metals, ICOM Committee on Conservation, Madrid 1972. Based on paper prepared at Institute for Archaeology, May 1971, 'An assessment of the use of benzotriazole'.

Sherwin Williams Chemicals Technical Bulletin 65-90 Cobratec 99. Sherwin Williams Chemicals, P.O. Box 5638, Cleveland, Ohio 44101

Application Data Sheet (108/9) Copper. Brass. Bronze. 'Benzotriazole: an effective corrosion inhibitor for copper alloys'. Copper Development Association Inc. 405 Lexington Avenue, New York, New York 10017

Hori, Tadashi 'Characteristics, use, and method of application of benzotriazoles'. Boshoku Gijutsu 1969 18 (9), 393-8 (Japan).

Walker, Robert 'Benzotriazole as a corrosion inhibitor for copper'. Anti-Corros. Methods Mater. 1970 17 (9), 9-10, 12-15.

Ladenburg, P., Ber. 9 219-223 (1876) (Beilstein XXVI, 38)

Boyer, J.H., 'Monocyclic triazoles and benzotriazoles'. Chapter V

in Volume 7; Heterocyclic Compounds, ed. Elderfield, Robert C., John Wiley & Sons, Inc. N.Y.

5 e.g. The Merck Index, 8th ed., 1968, p. 135

6 Nesmeyanov, A.A.; Babin, V.N., Fedorov, L.A., Rybinskaya, M.I.; Fedin, E.I., 'NMR studies of tautomerism of benzotriazole'. Tetrahedron 25 4667-70 (1969)

7 Perrin, D.D., Dissociation Constants of Organic Bases in Aqueous Solutions, Butterworth & Co. Ltd., London, 1965

8 Zincke, Th.; Arzberger, H. 'Ueber Azimidoverbindungen'. Ann. 249 350-372 (1888)

9 Tarasevich, N.I., 'New rapid gravimetric determination of silver. Analytical properties of bromoazimidobenzene'. Vestnik Moskov. Univ. 3, No. 10, 161-68 (1948) C.A. 44:5759i

0 Tarasevich, N.I. 'Determination of copper and silver by homogeneous precipitation with azimidobenzene'. Vestnik Moskov. Univ. 10 No. 10 Ser. Fiz. Mat. i. Estestven.Nauk No. 7 111-13 (1955)

1 Lomakina, L.N.; Tarasevich, N.I. 'Microchemical determination of copper with bromobenzotriazole'. Metody Analiza Redkikh i Tsvet. Metal. Sbornik 1956, 33-9; Referat. Zhur., Met. 1957 Abstr. No. 13693 C.A. 53; 1991b

2 Lomakina, L.N., Tarasevich, N.I.; Agasyan, P.K. 'Micropotentiometric determination of silver with triazoles'. Zavodskaya Lab. 24 270-3 (1958) C.A. 54; 10668d

3 Elbs, K, et al. Zur Kenntnis der Phentriazole J. Prakt. Chem., 2 108, 209 (1924)

4 Mansfield, Florian, Smith, Tennyson,; Parry, E.P. 'Benzotriazole as corrosion inhibitor for copper'. Corrosion 1971 27 (7) 289-94

5 Prall, J.K. Thesis, University of London, 1962 The Effect of Complex Ion Formation on the Polarization Potential and Nature of Electrodeposits of Copper with Particular Reference to Benzotriazole

6 Cotton, J.B.; Scholes, I.R. 'Benzotriazole and related compounds as corrosion inhibitors for copper'. Brit. Corros. J., 2 (1), 1-5 (1967)

7 Poling, G.W. 'Reflection infrared studies of films formed by benzotriazole on copper', Corros. Sci. 1970 10 (5) 359-70

Morito, Nobuyuki; Suetaka, Wateru 'Infrared and ultraviolet-visible reflection spectra of the surface films on copper treated with benzotriazole'. Nippon Kinzoku Gokkaishi 1971 35 (12), 1165-70 (Japan).

Angely, L., Bonnemay, M., Bronoel, G.; Peslerbe, G., 'Absorption of benzotriazole on copper'. Metaux 1971, 46 (555), 409-13 (Fr)

Remington, Ward Jepson Thesis, The Ohio State University 1937 The Influence of Hydrogen Ion Concentration on the Separation of Certain Metals with 8-hydroxy Quinoline and A Study of Benzotriazole as an Analytical Reagent. This reference is often given as: W.J. Remington and H.V. Moyer, Dissertation Abstract No. 24 Columbus, Ohio. Ohio State University Press 1937

Curtis, J. Alfred, Quantitative determination and separation of copper with benzotriazole'. Ind. Eng. Chem., Anal. Ed. 13 349-51 (1941)

Cheng, Kuang Lu 'Determination of silver with 1,2,3-benzotriazole'. Anal. Chem. 26 1038-40 (1956)

Canonica, L., De Leone, R.; Bersano, C., 'Complex salts of copper, nickel and cobalt with the triazoles'. Rend. ist. lombardo sci. PtI Classe Sci. mat. e nat. 87 276-8 (1954) C.A.49: 15592i

Akiyama, Tomoyuki; Terano, Yoshitake, 'Determination of silver and copper by 1,2,3-benzotriazole'. Kyoto Yakku Daigaku Gakuko No.12 53-5 (1964) (Japanese)

Inoue, Motomichi, Kishita, Michihiko; Kubo, Masaji 'Magnetic moments of dichloro(1,2,4 triazole) copper(II)'. Inorg. Chem. 4 (5), 626-8 (1965)

Havíř, J., 'Potentiometric determination of silver with 1,2,3 benzotriazole'. Collection Czech. Chem. Commun. 32 (1), 130-140 (1967) (German)

Gerenrot, Yu. E.; Eichis, A.P. 'Effect of benzotriazole on the electrodeposition of copper'. Zashch Metal 2 (5), 581-3 (1966) (Russ.) C.A.66: 34188v

Poddar, S.N.; Roy, K. 'Amperometric estimation of copper with 1,2,3-benzotriazole'. Indian J. Appl. Chem. 33 (3), 183-8 (1970)

Bates, R.G., Chapter 10, p. 401-2, 'Concept and Determination of pH,' in Treatise on Analytical Chemistry, Part I, Volume I, ed. I. M. Kolthoff and P. J. Elving, Interscience, New York 1959

Sharkey, J.B.; Lewin, S.Z., 'Conditions Governing the Formation of Atacamite and Paratacamite.' Amer. Mineral. 56 179-192 (1971)

Appendix

The appendix is arranged in two parts. Part I lists
ticles which have appeared since the reviews cited in the body
the paper, and a few related articles which have appeared
rlier. These are followed by a listing of patents and applications
ticles, arranged in categories modeled on those in references
) and (10). Part II lists an article and patents concerning
bstituted benzotriazoles used as corrosion inhibitors. While
me of these articles and patents do not bear directly and explicitly
this work, they do illustrate the broad range of uses and
rmulations for benzotriazole today. While many of these formu-
ations (and of those listed in earlier reviews) may never find
eir way into general use, it is quite probable that a recent
pper alloy object has been "treated" with benzotriazole whether
not there is any record of this having been done. This would
lso be true for earlier objects which have been cleaned or stored
protective papers or wrappings.

rt I Articles and Patents Relating to Benzotriazole

Cotton, J.B. 'Recent innovations in corrosion inhibition'. Scuola Azione 1965 (5), 115-36 (Ital) C.A. 63:15985a

Kinoshita, Hiroshi; Hayashi, Tadeo; Ishida, Takeo 'Radioactive study of the action of addition agents in the electrodeposition of metals. II Influence of sodium β-napthalene sulfonate and some additives in the electrodeposition of nickel from nickel plating solutions'. Denki Kagaku 34 184-9 (1966) (Japanese) C.A. 65:6728c

Kinoshita, Hiroshi; Higuchi, Shunichi; Hayashi, Tadeo; Ishida, Takeo; 'Adsorption behavior of addition agents used in copper electroplating studied by measuring the differential capacity of the electrical double layer'. Kinzoku Hyomen Gijutsu 17 (10), 389-94 (1966) (Japanese) C.A. 68:26229k

Nippe, M.W.; Fischer, H., 'Influence of interfacial active materials on the current-potential curve of copper'. Electrochim. Acta 12 (4), 369-94 (1967) (Ger.)

Tunturi, P.J. 'Benzotriazole as a copper inhibitor'. Kem. Teollisuus 1969, 26 (12), 975-8 (Finnish)

Bonora, Pier L.; Bolognesi, Gian Paolo; Trabanelli, Giordano; Zucchi, Fabrizio, 'Action of some corrosion inhibitors in neutral solution'. Ric. Sci. 1969 39 (2), 145-51 (Ital.)

Slizys, R.; Saboniene, E.; Mataulis, J. 'Changes in Cu^+ ions concentrations in sulfate, copper plating electrolytes containing certain additives'. Liet. TSR Mokslu Akad. Darb., Ser. B 1969, (3), 43-50 (Russ.) C.A. 72:27615c

Bonora, Pier L.; Bolognesi, Gian Paolo; Borea, P.A.,; Zucchini, G.L.; Brunora, G. 'Inhibition of copper corrosion in neutral solution'. Ann. Univ. Ferrara, Sez 5 1970 (pub 1971) Suppl. 5 685-97 (English)

Poling, George 'Films of oil oxidation products on copper'. J. Electrochem. Soc. 1970, 117 (4), 520-4

Ross, Thomas Kenneth; Berry, M.R. 'Benzotriazole as an inhibitor of the corrosion of copper in flowing sulfuric acid'. Corros. Sci. 1971, 11 (4), 273-4 C.A. 75:93804b

Walker, R.; Benn, R.C. 'Effect of benzotriazole on the hardness of copper electrodeposits'. Electrochim. Acta 1971, 16 (7), 1081-8 C.A. 75:93871w

Ushenina, V.F.; Klyuchnikov, N.G. 'Effect of some chelate-forming reagents on the corrosion of metals'. Zh. Prikl. Khim. (Leningrad) 1971 44 (1), 191-5 (Russ.)

Chin, Robert J.; Nobe, Ken, 'Electrochemical characteristics
of iron in sulfuric acid containing benzotriazole'.
J. Electrochem. Soc. 1971 118 (4), 545-8

AQUEOUS SYSTEMS

Free flowing collapsible capsule corrosion and leakage inhibitors.
Union Carbide Corp. Neth. Appl. 6,605,917, Oct. 31, 1966
U.S. Appl. April 30, 1965 C.A. 66:67671a

Organic phosphoric acid compound corrosion protection in aqueous
systems, Hwa, Chih Ming, S. African 68 03,379 22 Oct. 1968
U.S. Appl. 13 Jun 1967 C.A. 70:117988g

Corrosion inhibiting antifreeze. British Petroleum Co., Ltd.
Fr. 1,563,262 11 April 1969 Ger. Appl. 23 Mar. 1967
C.A. 72: 69017q

Anticorrosion agents for metals. Hajimi, Yumoto; Masahiro, Otsuka
Japan 70 21566 21 July 1970 Appl. 03 Oct. 1967 C.A. 74:60218q

Inhibiting corrosion in various circulating waters or water/glycol
systems. Tikkanen, Matti; Ylasaari, H.A.; Seppo, T.
Finn. 44, 315, 11 Oct. 1970, Appl. 12 June 1967
C.A. 76:89392u

Inhibiting the corrosion of metals in water systems with
epoxyethanepolyphosphonate compositions. Vandersall,
Howard L. (Monsanto Co.) U.S. 3,625,716 07 Dec. 1971
Appl. 13 Apr. 1970 C.A. 76:130545m

Improved antifreeze composition. Shell Internationale Neth.
Research Maatsch ppij N.V. Neth. Appl. 70 10,895
27 Jan 1971 Appl. 23 Jul 1970 C.A. 75:23651a

Additives for closed hot-water central heating systems. Muetzel,
Peter S. Ger. Offen. 2,122,068, 30 Dec. 1971, Brit. Appl.
01 May 1970. C.A. 76:117411v

FUNCTIONAL FLUIDS

Benzotriazole-barium sulfonates corrosion inhibitor for lubricants.
Farbewerke Hoechst A.G. Fr. 1 561 899 28 Mar. 1969
Ger. Appl. 13 May 1967 C.A. 72:45788r

Biodegradable lubricating emulsions. Zuraw, Charles L.; US 3507,792 21 Apr
1970, Appl. 30 Nov., 1967. C.A. 73:17175r

Effect of amine salts of dialkyl phosphites on the critical anti-
wear load. Sugai, Kyoichi; Watanabe, Shoji; Miyashige,
Akira; Moriyama, Masaru Yukagaku 1970, 19 (9), 910-14 (Japan)
C.A. 73:132693v

Protective compositions for the wires of paper making machines. Yusupov, V.I.; Meridian, Kh. I.; Guseva, M.F.; Doronina, M.A., U.S.S.R. 299 589, 26 Mar. 1971, Appl. 20 May 1969, from Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znoki 1971, 48 (12), 110. C.A. 75:89438t

Corrosion inhibiting compositions for functional fluids. Avery, Lowell R.; Conklin, Wayne A. U.S. 3,640,873, 07 Feb. 1972 Appl. 793,177 22 Jan. 1969 C.A. 76:115800x

DETERGENTS, CLEANERS, POLISHES

Tarnish-inhibiting dishwashing detergents. Samuel A. Heininger (Monsanto Chemical Co.) U.S. 2969,329 Jan 24 1961 C.A. 55:9915h

Metal Cleaning. Hill, Victor William; Ashdown, Ronald A. Brit. 1,129,337, 02 Oct. 1968 Appl. 10 Dec. 1965 C.A. 70:22483g

Acid cleaning of copper-containing products. Geigy, J.R., A.G. Fr. 1577 582, 08 Aug. 1969 Brit. Appl. 22 Jul. 1967 C.A. 72:103259g

Corrosion inhibiting chemical compositions [acids] for copper and its alloys. Popplewell, Alan F.; Finan, Michael A. Brit. 1,198,312, 08 Jul. 1970 Appl. 22 Jul. 1967 C.A. 73:69321e

Composition for inhibiting the corrosion of copper-based articles. Donaldson, Robert; Brit. 1,235, 468, 16 Jun. 1971 Appl. 07 Nov. 1967. C.A. 75:79774k C.A. 73:6728x

COATINGS, STORAGE AND PACKING

Multipurpose corrosion inhibitor compounds. Ruzevick, Peter M.; Adams, Ronald F.; Reynolds, Albert H. Fr. 1,508,668 05 Jan 1968, U.S. Appl. 24 Jan. 1966. C.A. 70:40298e

Preparation of anticorrosive wrapping paper. Scholes, Jan R.; Cotton, Joseph B. Ger. Offen. 1,807,353, 11 Sept. 1969 Brit. Appl. 06 Nov. 1967 C.A. 72:4496a

Anticorrosive film for metals. Kando, Masahiko; Sato, Isao, Japan 70 01,330, 17 Jan. 1970. Appl. 04 Aug. 1967

Vapor phase corrosion inhibitor. Kando, Masahiko; Sato, Isao Japan. 70 01,735, 21 Jan. 1970. Appl. 04 Aug. 1967

Wrapping material containing 3-amino-1,2,4-triazole as corrosion inhibitor for metals. Moyer, Wendell W., Jr.; Ilagen, Perlita A. Ger. Offen. 1,927,725, 30 Apr. 1970, U.S. Appl. 06 Aug. 1968

ELECTROLYTIC PROCESSES

Destroying cyanide or acid residues on surfaces of copper, brass or silver and preventing tarnishing of the surfaces. Lancy Laboratories, Inc. Brit. 1,120,675, 24 Jul. 1968, U.S. Appl. 12 Jul 1966

OTHER APPLICATIONS

Hansen, R.H.; De Benedictis, T.; Martin, W.M. 'Stabilization of polypropylene'. Polymer Eng. Sci. 5 (4), 223-6 (1965)

Tarnish resistant glass mirrors. John Mathews & Co. Ltd (by Thomas E. Johnson) Brit. 1.057.871. Feb. 8, 1967, Appl. May 9, 1962. C.A. 66:88347q

Stabilization of poly(4-methyl-1-pentenes) by benzotriazole in the presence of copper. Marshall, Brian A. Brit. 1,133,551, 13 Nov. 1968 Appl. 17 Feb. 1967. C.A. 70:38526j

Removal of metal impurities from Kerosine. Ford, Peter J.; Ger. Offen. 1,946,690 02 Apr. 1970 British Appl. 16 Sept 1968 C.A. 72:123697b

Flux for capillary soldering. Bergman, Axel H. Ger. Offen. 1963 965 09 Jul. 1970 Swed. Appl. 23 Dec. 1968 C.A. 74:129865t

Adhesives for the adhesion of glass and metal. Igashima, Takeshi; Kato, Yoshimitsu. Japan. 71 01,718, 16 Jan. 1971, Appl. 31 Jul. 1967; C.A. 76:14400e

Printing fabrics in gold and silver shades. Keino, Goro; Nakato, Kunihiro. Japan. 71 07,237, 23 Feb. 1971, Appl. 15 Nov. 1968. C.A. 76:473025j

Crosslinkable polyethylene resin compositions containing benzotriazole. Maruyama, Hiroyoshi; Hisahara, Tadaaki; Takahashi,Nobuo Japan. 71 10,229 16 Mar. 1971, Appl. 20 Apr. 1967. C.A. 76:60518d

Copper/poly(arylene sulfide) laminates. Blackwell, Jennings P. U.S. 3,616,186 26 Oct, 1971, Appl. 26 Sept. 1969 C.A. 76:60578

Corrosion inhibitors for alkanolamine solutions used to absorb acidic gases from gas streams. Mago, Blake F.; West, Charles William. Ger. Offen. 2,134,798, 27 Jan 1972 U.S. Appl. 054,595, 13 Jul 1970 C.A. 76: 129691z

Part II Substituted Benzotriazoles - Corrosion Inhibitors

Lane, E.S.; Williams, C. 'Organic complex-forming agents for metals. I Preparation of 4-hydroxy and 4,7-dihydroxybenzimidazoles and related compounds'. J. Chem. Soc. 1956 569-73

1,2' Bi-benzotriazole compounds. Harder, Robert J., to E.I. du Pont de Nemours & Co. U.S. 3,184,471, May 18, 1965, Appl. Jan 17, 1963 C.A. 63:4305g

Preparation of 5-substituted benzotriazoles. J.R. Geigy, A.G. Neth. Appl. 6 414 144, June 8, 1965, Brit. Appl. Dec. 6, 1963, Jan. 24, 1964 C.A. 63:18103h

Bis(benzotriazoles) as corrosion inhibitors. J.R. Geigy, A.G. Fr. 1 446 545, July 22, 1966, Brit. Appl. Aug 14, 1964, C.A. 66:116801d

4,5,6,7,-Tetrahydrobenzotriazole as a corrosion inhibitor for metals. Geigy, J.R., A.G. Fr. 1,577,580, 08 Aug. 1969 Brit. Appl. 21 Jul. 1967 C.A. 72:11480n

4-hydroxybenzotriazoles as corrosion inhibitors and metal deactivators. Geigy, J.R., A.G. Fr. 1 577 581, 08 Aug. 1969 Brit. Appl. 21 Jul 1967 C.A. 72:90477z

Anticorrosive 1-hydroxy-1-H benzotriazoles. Randell, Donald R.; Hargreaves, James R. Ger. Offen. 2 003 827, 30 Jul 1970 Brit. Appl. 29 Jan 1969 C.A. 66:66583f

Benzotriazoles from N-hydroxybenzotriazoles. Randell, Donald R.; Hargreaves, James R. Ger. Offen. 2,003,828, 30 Jul 1970 Brit. Appl. 29 Jan 1969 C.A. 73:66585h

Benzotriazoles from 1-hydroxybenzotriazoles. Randell, Donald R.; Hargreaves, James R. Ger. Ofeen 2 003 860, 06 Aug 1970 Brit. Appl. 29 Jan 1969 C.A. 73:77250w

4,5,6,7-Tetrahydrobenzotriazoles for use as corrosion inhibitors. Butula, Ivan. Ger. Offen. 1,948,794, 01 Apr 1971 Appl. 26 Sept 1969

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-B15465

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